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The effect of pulping concentration treatment on the properties of microcrystalline cellulose powder obtained from waste paper

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ABSTRACT

Microcrystalline cellulose (MCC) powder was isolated from three grades of waste paper: book, Groundwood/Newsprint and paperboard, through the processes of pulping and hydrolysis. Pulping treatment on these grades of waste paper was done using varying concentrations of caustic soda. Effects of the concentration of the pulping medium on the thermal and kinetic properties were investigated. Also determined were the effects of this on the physico-chemical properties. The chemical structure was characterized using an infrared spectroscopy (FTIR). Results showed these properties to be affected by the concentration of the pulping medium.

1. Introduction

Microcrystalline cellulose (MCC) is a partially depolymerised non-fibrous form of cellulose which mainly appears as a white, odourless, tasteless and crystalline powder (Westermarck, Juppo, Kervinen, & Yliruusi, 1999). It finds extensive use in the cosmetic, food, pharmaceutical and plastic industries (Ejikeme, 2008). It is a versatile excipient employed frequently in extrusion–spheronization owing to its intrinsic properties when wetted with water (Mascia, Seiler, Fitzpatrick, & Wilson, 2010).

However, physical pre-treatment (such as pulping, regeneration and pulverization) can significantly modify microcrystalline cellulose properties, which results in different moisture absorption capacity (Adel, Abd El-Wahab, Ibrahim, & Al-Shemy, 2011). Tsoumis (2010) reported the use of pulping process as a veritable pre-treatment method in the paper recycling process. Chemical pulping process could be of three major types namely: Kraft, soda and sulfite (EPA, 2010). The properties of microcrystalline cellulose have been shown to be affected by the conditions of hydrolysis (El-Sakhawy & Hassan, 2007).

Since cellulose obtained from different sources differ slightly in properties such as: crystallinity, moisture content, surface area, porosity and molecular weight, etc. There exists therefore, a possibility that with different pre-treatment conditions, differences in properties of microcrystalline cellulose powder isolated from similar sources could be obtained.

On the other hand, various grades of paper exist. These grades are as a result of the variations in the properties of these paper, such as: the type of fibre used in the papermaking process, method of pulp preparation (mechanical or chemical), as well as the additives used in the papermaking process as reported by Britt (2010) and Carpenter and Leney (1952). Identification of these differences is done based on standard test methods.

This paper therefore takes a comparative study of the properties of microcrystalline cellulose powder obtained from three grades of paper: Book paper, Groundwood/Newsprint and Paperboard to ascertain any differences resulting from different pulping pre-treatment process conditions.

2. Materials and methods

2.1. Materials

Three paper grades (Book paper; Groundwood & Newsprint paper; and Paperboard). Reagents used were obtained as pure grades, namely: sodium hydroxide pellets (96% (w/w)) (from BDH), sulphuric acid from BDH (98% (w/w)), sodium hypochlorite (5.3% (w/w)), hydrogen peroxide (30% (w/w)), acetone, ethanol, toluene, xylene (95% (w/w)) supplied by Analar, dimethyl sulphoxide (60% (w/w)) and distilled water.

2.2. Method

The methods adopted for this work include pulping, de-inking, cellulose digestion, cellulose drying, acid hydrolysis, thermal

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analysis and physico-chemical property tests. These methods were carried out at the reactions and particulate systems laboratories of the Chemical Engineering Department, University of Port Harcourt, Nigeria.

2.3. Soda pulping

50 g each of shredded paper samples (Book paper, Newsprint/Groundwood, and Paperboard) were measured into a 1000 ml capacity beaker. At each batch, 500 ml of two different concentrations of NaOH 5% and 20% (w/w) were added amidst vigorous agitation. At different experiments, the contents were digested at a temperature condition range of 293–353 K and 1 atm for 180 min in a constant water bath. This pre-treatment was done in order to eliminate fillers, additives and other impurities associated with waste printers' paper.

2.4. De-inking process

Alongside the soda pulping process, 150 ml of NaClO (5.3% (w/w)) and 150 ml of H_2O_2 (30% (w/w)) were added to the content of the cellulose pulp at the same temperature and pressure condition, for the purpose of de-inking and also to offset the evident yellow colouration of the pulp. A surfactant was also added alongside. A frothy scum was formed on the surface of the content. The resulting mixtures were blue–black, pale green and deep brown coloured liquor for the Book paper, Newsprint/Groundwood and Paperboard grades respectively. The residues were filtered off and washed repeatedly with distilled water to a neutral pH and dried in an automatic oven at 342 K and 400 mmHg for a period of 1 h. The recovered dry pulped residues (cellulose) were weighed and coded as A_1, B_1, C_1 and A_2, B_2, C_2 in line with the 5 and 20% (w/w) pulping concentration treatments respectively.

2.5. Acid hydrolysis of cellulose pulp

The obtained cellulose was subjected to hydrolytic action of 150 ml quantity of H_2SO_4 (15% (w/w)) in a 500 ml capacity beaker. The mixtures were frequently stirred and kept in a constant temperature water bath operating at 373 K for 30 min. The hot mixtures were washed repeatedly with distilled water in a 1000 ml capacity beaker. The residues were collected by filtration, dried at 342 K for 1 h, weighed, pulverized and stored in separate airtight containers in a desicator.

2.6. Kinetic and thermodynamic data parameter estimation

At each experiment, the corresponding percentage weight loss was determined. Using the Coats–Redfern equation, thermodynamic parameters such as E^*, A, ΔS^*, ΔH^*, ΔG^*, were determined for the pulping process

$$\log\left[\frac{\log\left(\frac{W_f}{W_f - W}\right)}{T^2}\right] = \log\left[\frac{AR}{\phi E^*}\left(1 - \frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.303RT}$$

where W_f and W are the residual and initial weight of the sample respectively up to temperature T. R is the gas constant, E^* is the activation energy, ϕ is the heating rate and $(1 - 2RT/E^*) \cong 1$. The plot of the LHS of the above equation against $1/T$ gives a slope. The pre-exponential factor (A) and activation energy E^* were determined from the intercept and linear slope of the plot of each stage respectively. Other kinetic parameters: Enthalpy of activation (ΔH^*), the entropy of activation (ΔS^*), and the free energy of activation (ΔG^*) were calculated using this relationship:

$$\Delta H^* = E^* - RT;\ \Delta G^* = \Delta H^* - T\Delta S^*;\ \text{and}\ \Delta S^* = 2.303\left(\log\frac{Ah}{kT}\right)R$$

where (k) and (h) are Boltzman and Planck constants respectively.

Table 1
Yield of cellulose sample at various stages of experiment.

Sample	Weight of dry sample (g)			Yield (%)
	Initial	After pulping	After hydrolysis	
A_1	50	41.02	40.86	81.72
A_2	50	22.25	21.75	43.50
B_1	50	13.25	13.01	26.02
B_2	50	5.80	5.75	11.50
C_1	50	27.35	27.29	54.58
C_2	50	25.14	25.08	50.16

Hint: A_1, A_2 implies Book paper pulped (pre-treated) with 5% and 20% (w/w) NaOH respectively.
B_1, B_2 implies Groundwood/Newsprint pulped (pre-treated) with 5% and 20% (w/w) NaOH respectively.
C_1, C_2 implies Paperboard pulped (pre-treated) with 5% and 20% (w/w) NaOH respectively.
Note: all results presented were the mean of two determinations.

2.7. Physico-chemical property tests

Some of the properties determined were pH, solubility, density, porosity, compressibility, and moisture sorption capacity, loss on drying, intrinsic viscosity, and crystallinity index using the methods of Uyigue and Okwonna (2013).

2.8. FTIR spectra analysis

Fourier infrared spectra were recorded using a Schimadzu IR prestige. The samples were measured as thin films using the diffuse reflectance mode of IR spectroscopy. By vibratory mechanism, chemical bonds present in the sample were identified as the peaks in the resulting infrared spectrum measured at specific wave number and percentage transmittance of the infrared rays. Actual chemical bonds associated with the peaks were identified with the aid of a standard FTIR spectra absorption data on the basis of stretching and bending frequencies. Bands were recorded in the region from 4000 to 400 cm^{-1}.

3. Results and discussion

Generally, high pulping concentration pre-treatment resulted in low yield of the cellulose (Table 1). Groundwood/Newsprint (Sample B) gave the least cellulose yield, while the effect of concentration change on the yield of cellulose with Paperboard (sample C) was marginal. Book paper (Sample A_1) gave the highest yield at the least concentration (5% (w/w)). This implies that very high pulping concentration may not favour cellulose yield.

Coats–Redfern plot is shown in Fig. 1. Table 2 shows the calculated values of E^*, A, ΔS^*, ΔH^* and ΔG^*, for the pulping process at 353 K. Inspection of the data reveals that the reaction was exothermic and very large amount of heat, dissipated in the process as shown by the (ΔH^*) values. Negative entropy change (ΔS^*) values shows the improved crystallinity (Table 3) of the obtained microcrystalline cellulose as compared to the original paper grade sample source in accordance with the work of Seleem, El-Inany, El-Shetary, Mousa, and Hanafy (2011). Moreover, these values showed a general increase in disorder within the MCC structure with increased pulping concentration. Endergonic (non-spontaneous) nature of the pulping reaction process were indicated by the ΔG^* values.

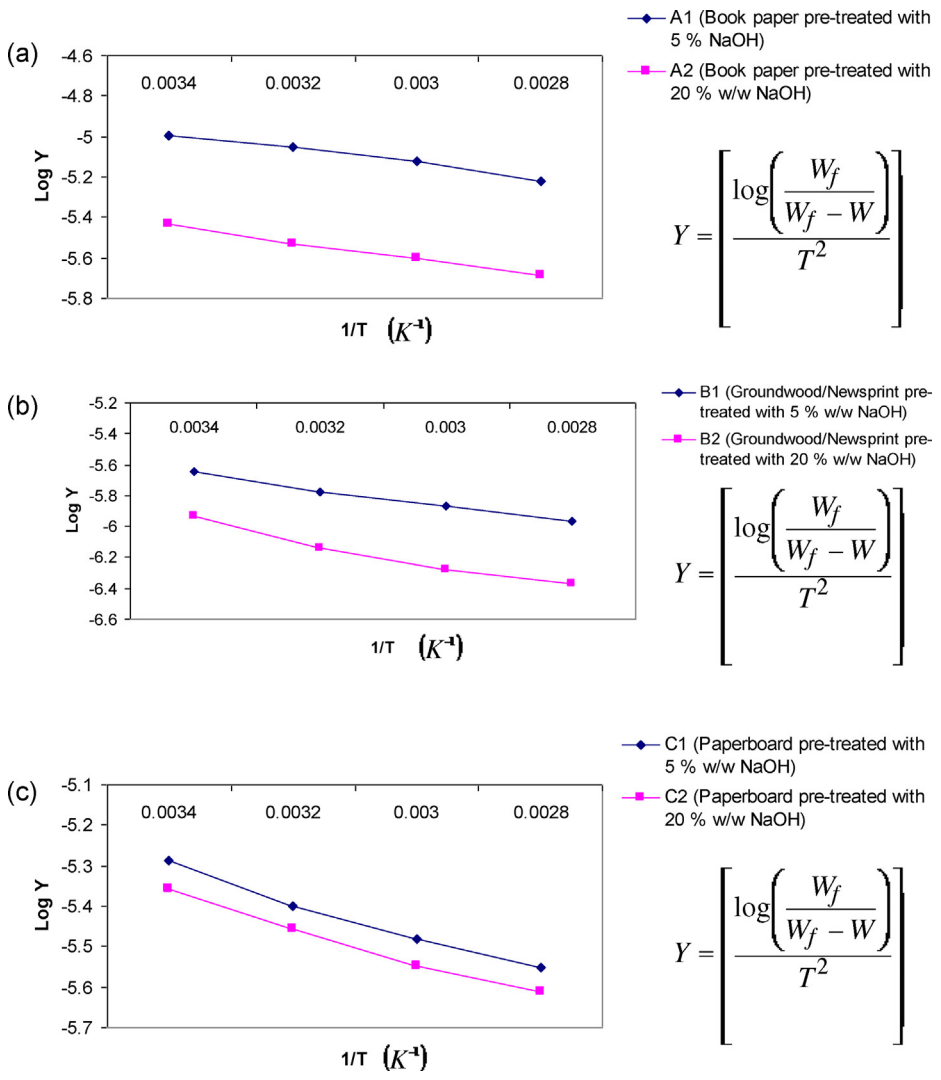

Fig. 1. Coats–Redfern plot of MCC from (a) Book paper, (b) Groundwood/Newsprint, (c) Paperboard.

High pulping concentration pre-treatment condition could have resulted in an increased amount of associated energy available for the paper recycling process. Furthermore, moderate values of E^* shows moderate reaction rate of the entire pulping process.

The effect of reagent concentration on the MCC appearance was negligible. However, other physico-chemical properties such as density, porosity, loss on drying, intrinsic viscosity, degree of polymerization, crystallinity index were affected by the concentration of the pulping reagent as shown in Table 3.

The wide variation in moisture sorption values between MCC obtained from the same paper grade shows that high pulping concentration could have exposed more amorphous regions within the MCC structure in accordance with the work of Ejikeme (2008). The lack of hydrogen bonding in these amorphous portions, make them serve as potential sites for interaction with water molecules. Large surface area and internal porosity are other reasons for this (Dukic'-Ott, Thommes, Remon, Kleinebudde, & Vervae, 2009).

The FTIR spectra were carried out to characterize the chemical structure by identifying the functional groups present in each sample. The absolute absorbance of different bands was determined and the fingerprints of all the MCC samples were similar (Fig. 2). Table 4 shows the intensity at different band positions.

Table 2
Thermodynamic and kinetic parameters of obtained microcrystalline cellulose at 353 K.

Sample	ΔE^* (kJ mol^{-1})	A (s^{-1})	ΔS^* (kJ mol^{-1} K^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})
A_1	510.3	-1.8004×10^{-6}	−38.7998	−2424.52	11,271.8094
A_2	560.99	-7.8569×10^{-7}	−31.9046	−2373.85	8888.4738
B_1	723.88	-8.7138×10^{-7}	−32.7654	−2210.96	9355.2262
B_2	982.07	-9.0869×10^{-7}	−33.1140	−1952.77	9736.4720
C_1	590.73	-1.2203×10^{-6}	−35.5657	−2344.11	10,563.5801
C_2	583.30	-1.0213×10^{-6}	−34.0855	−2351.54	9680.6415

Hint: A_1, A_2 implies Book paper pulped (pre-treated) with 5% and 20% (w/w) NaOH respectively.
B_1, B_2 implies Groundwood/Newsprint pulped (pre-treated) with 5% and 20% (w/w) NaOH respectively.
C_1, C_2 implies Paperboard pulped (pre-treated) with 5% and 20% w/w NaOH respectively.

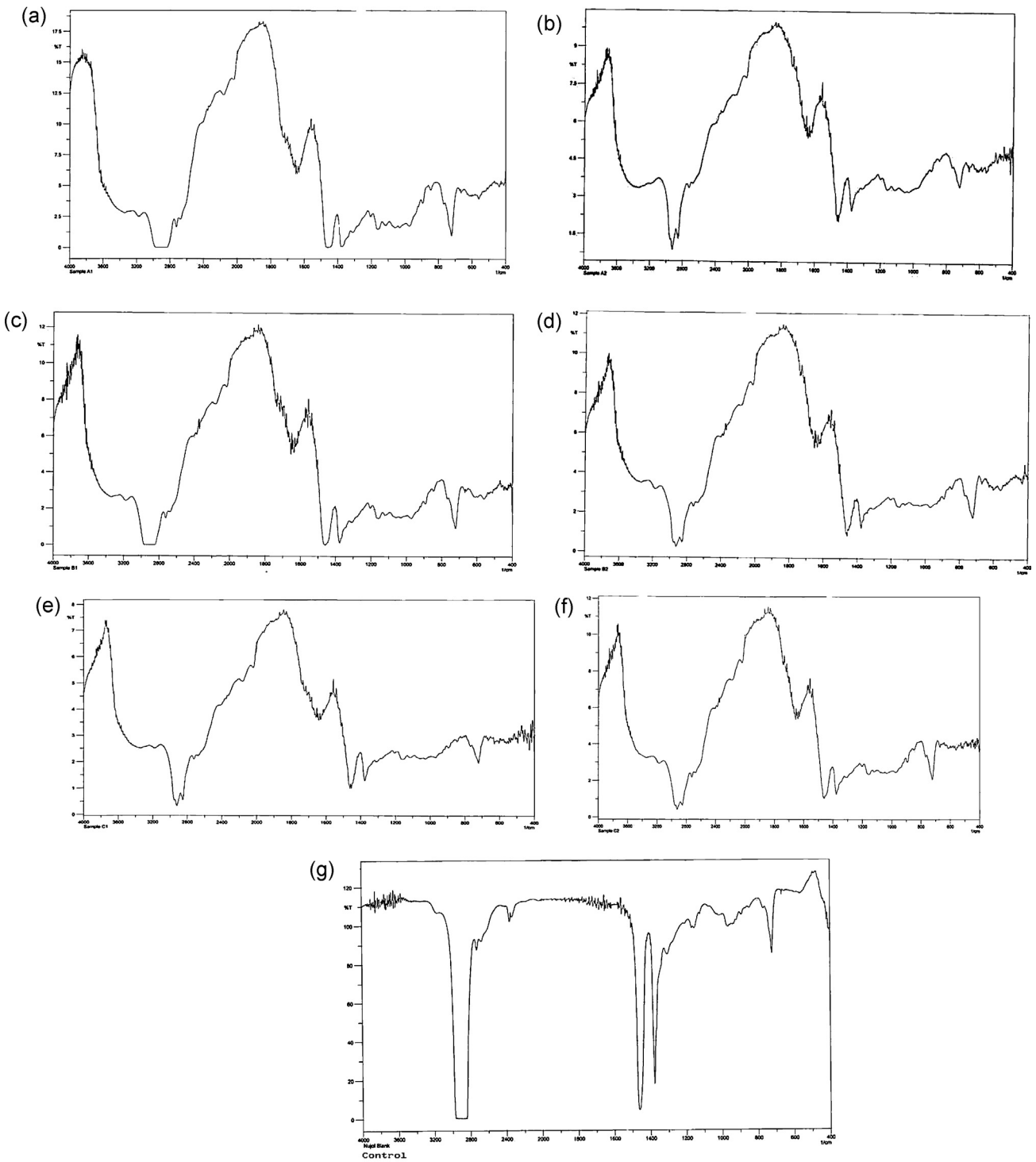

Fig. 2. FT-IR spectrum of (a) cellulose sample A_1 obtained from Book paper; (b) cellulose sample A_2 obtained from Book paper; (c) cellulose sample B_1 obtained from Groundwood/Newsprint; (d) cellulose sample B_2 obtained from Groundwood/Newsprint; (e) cellulose sample C_1 obtained from Paperboard; (f) cellulose sample C_2 obtained from Paperboard; (g) control (Nujol blank sample).

The band at 3300–3500 cm^{-1} was due to the intermolecular and intramolecular O—H stretching. Its absorbance intensity decreased upon the hydrolysis of the various paper grade samples. The band at 2960–3100 cm^{-1} was due to the C—H band stretch. Ester stretch was observed as follows: 1750–1800 cm^{-1} for C—O stretch and 1480–1530 cm^{-1} for C—O—C stretch. The shoulder at 1450–1400 cm^{-1} was due to C—C bonds. The decrease in intensities of bands related to —CH or $—CH_2$ vibrations (1390, 1180, 1060 cm^{-1}) indicate an increase of the oxidation degree. The approximate peak at 849.97 cm^{-1} was associated with the C—H out of plane ring stretching in cellulose due to β-glycosidic linkages. The decrease in the intensity after this point could be associated with the increase in crystallinity of the obtained MCC samples.

These values varied with concentration of the pulping medium.

Table 3
Physico-chemical properties of MCC obtained from different waste printers' paper grades.

Properties	MCC from Book paper		MCC from Groundwood/Newsprint		MCC from Paperboard	
	Sample A_1	Sample A_2	Sample B_1	Sample B_2	Sample C_1	Sample C_2
Appearance						
Colour	Whitish	Whitish	Off-white	Off-white	Dull-white	Dull-white
Odour	Odourless	Odourless	Odourless	Odourless	Odourless	Odourless
Taste	Tasteless	Tasteless	Tasteless	Tasteless	Tasteless	Tasteless
Average particle size (μm)	≤250	≤250	≤250	≤250	≤250	≤250
Density ($g\,cm^3$)						
True	1.91	1.90	1.68	1.67	1.38	1.44
Bulk	0.42	0.45	0.36	0.38	0.28	0.33
Tapped	0.56	0.63	0.45	0.50	0.38	0.42
Porosity (%)	78.1	76.4	78.6	77.3	79.7	77.1
Moisture sorption capacity (%)	3.5	4.1	5.6	5.9	12.4	13.5
Loss on drying (%)	4.8	4.5	5.0	5.1	5.6	5.8
Intrinsic viscosity (cm^3/g)	0.82	0.80	0.79	0.81	0.78	0.74
Degree of Polymerization	207	200	196	202	195	186
Crystallinity Index (%)	78.1	77.9	76.9	76.6	71.9	71.6

All results presented were the mean of two determinations.
Source: Uyigue and Okwonna (2013).

Table 4
Infrared spectra, intensity, and assignments of different bands for the obtained cellulose samples.

Band position (cm^{-1})	Intensity						Band assignment
	A_1	A_2	B_1	B_2	C_1	C_2	
3400	3.1	3.4	2.8	3.7	2.6	3.4	O—H stretch
3000	0.6	3.2	1.0	2.0	2.0	2.0	C—H stretch
1780	15	9.8	10.5	10.6	6.7	10.2	C—O stretch
1500	5	5.2	4.2	4.6	3.3	3.6	C—O—C stretch
1390	1.3	3.0	0.6	2	1.7	2.0	C—H deformation
≈900	3.7	4.2	2.3	2.7	2.6	3.1	Stretch of the β-glycosidic linkages

4. Conclusion

Paper provides an interesting alternative for the isolation of MCC. The effect of concentration change of the medium on cellulose yield of Paperboard (Sample C) was marginal, as compared to those obtained from Book paper and Groundwood/Newsprint (Samples A and B), where significant changes in the yield values were observed. Furthermore, the concentration of the pulping medium has been shown to affect the density, moisture sorption capacity, loss on drying, degree of polymerization, porosity, and thermal stability of the obtained MCC as well as the morphology of the fibres. From the results of this study, the lower concentration (5% (w/w)) of the pulping medium (NaOH) is therefore recommended as the optimal condition for isolation of MCC from these grades of waste paper.

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