Carboxymethyl cellulose from cavendish banana peel as a drag reduction agent

H Kaur¹*, A Japper-Jaafar¹, S Yusup²

¹Department of Mechanical Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia.
²Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia.

*harvingurchran@gmail.com, harvin_10663@utp.edu.my

Abstract. Reducing drag is reducing frictional pressure loss under turbulent flow conditions and can be achieved with addition of additives. These additives such as small amount of polymer can dramatically affect the turbulent structures of the flowing fluid and increase the flow rate. Synthetic polymers which are widely employed harm our environment when used excessively. A biopolymer is then sought for such purpose which is produced by living organisms and they are fairly shear stable and biodegradable. A biopolymer, derived from the Cavendish banana peel, was synthesized in this study. The polymer was converted to carboxymethylcellulose by etherification process. The drag reduction was assessed in this study using a rheometer where a reduced produced torque was perceived as a reduction of drag. The biopolymers produced were then rheologically characterized where the viscoelastic effects produced by these biopolymers were utilized to explain the drag reduction phenomena. The findings show that the biopolymer, synthesized at the right conditions, is capable of drag reduction up to 40% demonstrating the potential of the biopolymer from the green Cavendish banana peel at drag reduction when dissolved in water. The biopolymer synthesized at reaction temperature of 50°C and NaOH concentration of 40% works best at drag reduction.

1. Introduction

Drag reduction is observed as a reduced frictional pressure loss under turbulent flow conditions which will then substantially increase the flow rate of the fluid. Practical applications include water flooding systems, firefighting, agricultural spraying, and pipeline transport and drainage systems. In cases of heavy rain, for instance, existing drainage systems may not be able to cope with the amount of water introduced in the system and is further worsened with the accumulation of mud, leaves and other debris. Drag reduction agents can be introduced to increase the flow rate of water, reducing the water accumulation in the system and subsequently lessen the possibility of heavy flooding.

Widely studied polymers are usually employed to reduce drag. In a vessel, when a small amount of polymer is added, it can substantially reduce drag that the fluid has created. The important aspect of the polymers are that they possess a high molecular weight in terms of content of cellulose, chain flexibility and long linear chain structure. Most polymers are derived from petroleum and based on the chemistry of carbon, although some polymers have non-carbon based compounds.

An organic biopolymer produced by living organisms, such as polysaccharide, is a macromolecule. Cellulose is the most common organic compound and biopolymer on Earth where about 34% of all plant
matter is cellulose. It is synthesized in vivo through polymerization of glucose units and association of chains by the actions of syntheses. Functionalized cellulose is strategic in the developments and applications of new biomaterials where it could be converted by etherification [1], [2]. Carboxymethylcellulose (CMC) is a copolymer of two units: B-D-glucose and B-D-glucopyranose 2-O-(carboxymethyl)-monosodium salt, not randomly distributed along the macromolecule, which are linked via B-1, 4-glycosidic bonds. It is an anionic polyelectrolyte prepared by reaction of sodium chloroacetate with alkali cellulose. CMC is non-toxic and soluble in water when the degree of substitution is higher than 0.5 [3]. It has a thickening effect, film-forming ability and excellent behavior as protecting colloid and adhesive [9] as well as shear stable. Most of the CMC applications are due to its rheological properties. The ability of CMC to function as a thickener or flow-control agent depends largely on its degree of substitution, the molecular weight, and also on the relative stiffness of the cellulose backbone. The number of substituted hydroxyl groups per monomeric units is known as the degree of substitution (DS). [4] reported that the DS of CMC depends upon the sodium hydroxide concentration, reaction temperature and reaction time. The solubility of CMC tends to increase with increasing DS [5].

Based on research conducted, between corn cobs, sugarcane bagasse, wheat straw, banana peel and durian husk, the highest two biopolymers that contain the most cellulose are the banana peel and durian husk, the only limitation with durian husk is that the durian fruit is seasonal and not produced all year round. Cellulosic polysaccharides can be isolated from banana. Banana peels which sums up to 40% of the total weight of fresh bananas are underutilized [6]. By synthesizing the banana peel and converting it into Carboxymethylcellulose, the banana peel can be utilized. The potential applications of banana peel depend on its chemical composition and the important functional components of banana peel are the Resistant Starch (RS) and dietary fiber [7]. To produce a high amount of Carboxymethylcellulose, a banana peel should have a high content of fiber and carbohydrates with low levels of lignin [8]. [9] performed a study to compare the compositions of ripe and unripe Banana peel flours from the Cavendish (Musa acuminate L. cv. Cavendishii) and Dream (Musa acuminata colla AAA cv. Berangan) bananas and found that the green Cavendish banana peel has the highest carbohydrate level and crude fiber. The moisture content of the ripe banana peel ranges from 9.21% to 11.20% and was higher than that for unripe Banana peel [9]. This difference could be due to differences in varieties of bananas and processing parameters used. The crude fat contents of the peels were moderate (4.81%- 5.96%), and the carbohydrate contents of the peels ranged from 54.01% to 60.81%). The higher carbohydrate content of green banana peels could be related to its relatively low moisture content [9]. The high carbohydrate content is expected, as banana is known to contain sugars, starch and dietary fibers [9]. From this study, it can be concluded that the Cavendish green banana peel has a high carbohydrate level and crude fiber. The work presented in this paper focuses on the synthesis of modified cellulose from green Cavendish banana peel. The degree of substitution (DS) is varied during the synthesis by varying the sodium hydroxide concentration, reaction temperature and reaction time.

2. Methodology

2.1. Materials
The Cavendish green banana peel was utilized in this study. The chemicals used in the preparation and analysis of the carboxymethylcellulose (CMC) from the banana peel were purchased from Avantis Sdn. Bhd., Malaysia with 99% purity. They were of Analytical Reagent (AR) grade or equivalent as the AR grade had a higher purity than the standard laboratory reagent (SLR). The chemicals were sodium hydroxide, isopropanol, 90% ethanol, absolute methanol and sodium monochloroacetate. The water utilized as the solvent in the drag reduction assessment was the tap water obtained from the Universiti Teknologi PETRONAS (UTP) laboratory.
2.2. Synthesizing of CMC
The method of synthesizing the Carboxymethylcellulose (CMC) was adopted from the method employed by the Centre of Excellence for Polysaccharides Research, Friedrich Schiller University of Jena, Germany [10]. This method was chosen as it utilized the least amount of chemicals and relied mostly on the organic raw material. In this study, a total of 27 samples were synthesized under different parameter combinations.

2.3. Extraction of Cellulose
Banana peel was rinsed with tap water and sun-dried for 4 days. The dried peels were cut into small pieces below 20 mm using a Cole Parmer mortar grinder. It was then cooked with NaOH at 100°C for 3 hours on a magnetic stirrer at a constant speed of 200 rpm. The black slurry obtained was then filtered and washed with water for three times. The residue was dried in an oven at 55°C for 24 hours which resulted in pulps. The pulp was subsequently washed with water, filtered and dried again at 55°C for another 24 hours. The dried pulps were grounded into powder with an average size of 1 mm and stored in polyethylene bags to maintain minimal moisture content.

2.4. Synthesis of Carboxymethylcellulose from Banana peel
About 15.0g of cellulose powder from the steps above, 50ml of various concentrations of NaOH (20, 40 and 60%) and 450ml of isopropanol were mixed under an overhead stirrer in the beaker for 30 minutes at 200 rpm. The carboxymethylation reaction was initiated by adding 18.0g of monochloroacetic acid. The sample mixture was then covered with aluminium foil to avoid evaporation and heated up to the desired reaction temperature (50°C, 55°C and 60°C) in an oven for a variation of reaction time (60 minutes, 150 minutes and 240 minutes). The mixture was separated into the liquid phase and solid phase using a sieve. The liquid phase was removed and the solid phase was suspended in 100ml of methanol (70%v/v), neutralized with glacial acetic acid and filtered.

The final product was rinsed five times by suspending it in 300ml of ethanol (70%v/v) for 10 minutes to remove any undesirable by-products, and washed with 300ml of absolute methanol before being filtered for the next cycle of rinsing. The residue from filtration was dried at 55°C in the oven for 24 hours to obtain the final product: the Carboxymethylcellulose.

2.5. Degree of Substitution (DS)
The degree of substitution (DS) of CMC is the average number of hydroxyl group in cellulose structure which is substituted by carboxymethyl and sodium carboxymethyl group at C—2, C—3 and C—6. The DS of the CMC sample was determined using a standard ASTM method (D1439-94) known as the back titration method. The DS value is determined via:

\[ A = \frac{BC-DE}{F} \]  

\[ \text{Degree of Substitution} = \frac{(0.162)xA}{1-(0.058xA)} \]  

where A is the Mili-equivalents of consumed acid per gram of specimen, B is the Millimeters of added sodium hydroxide, C is the Normal sodium hydroxide, D is the Millimeters of consumed hydrochloric acid, E is the Normal hydrochloric acid and F is the Specimen gram used.

2.6. Drag reduction assessment
A standard sample preparation procedure was adopted where a 100 ppm of banana peel CMC was mixed with UTP tap water. An overhead stirrer was used with a constant low speed around 200 rpm for a duration of 3 hours to ensure the biopolymer was well mixed with water. Once the mixing was completed, the polymer solutions appeared to be visibly homogeneous and the beaker was sealed to
avoid water loss by evaporation which caused an increase of concentration in the solution. Solutions were then left for at least 8 hours to ensure complete de-aeration.

To load the solution onto the controlled stress rheometer, a pipette is utilized. Once the sample was placed into the double concentric cylinder geometry on the rheometer, the solution was left to rest for 2 minutes to ensure that the molecules were sufficiently relaxed after the high shear applied during loading. A method adopted from [11] was utilized for the drag reduction assessment. A strain sweep step was performed from 0 rad/s to 300 rad/s (the maximum attainable limit by the rheometer) and the torque was monitored under the imposed angular velocity. The temperatures for all the assessments were maintained constant at 25°C with the gap within the geometry set to 2000 micron. All measurements were repeated at least three times to confirm repeatability and only a representative data sample was presented. The repeatability was found to be within 10%.

The drag reduction ability was assessed under a controlled stress rheometer by measuring the difference of the flow curves (torque vs. speed) of a treated solution to untreated solution. Any reduction in torque was believed to be contributed by the drag reduction mechanism and the drag reduction percentage can be calculated via

$$DR\% = \left[\frac{T_u - T_t}{T_u}\right] \times 100$$

(3)

where:

- $T_u$: Torque obtained with the untreated fluid, N.m
- $T_t$: Torque obtained with the treated fluid (addition of CMC), N.m

A double concentric cylinder is the geometry utilized for the drag reduction assessment where the inner cylinder will rotate to induce shear. The Reynolds number equation corresponding to this geometry, $Re$, is given by

$$Re = \frac{\Omega \rho R_m (\Delta R)}{\mu}$$

(4)

where $\Omega$ is the angular velocity (rad/s), $\rho$ is the fluid density (kg/m$^3$), $R_m$ is the moving cylinder radius of the rheometer (m), $\Delta R$ is the difference between the outer and inner cylinder radius (m) and $\mu$ is the fluid viscosity (Pa.s).

3. Result and Discussion

Twenty-seven samples of the green Cavendish banana peel CMC are synthesized with different parameter combinations. However, only selected representative samples are discussed in this paper for simplicity. Similar observations could be deduced from other samples.

3.1. Polymer characterization

The biopolymer that is characterized has been synthesized with a reaction time of 150 minutes, reaction temperature of 50°C and NaOH concentration of 40%. This sample is chosen at random for the characterization.

The X-ray diffraction (XRD) results indicate that the highest peak is the cellulose with d values of 7.33741, 5.38695 and 3.89250. The second highest component is the polysaccharide with d values of 4.55430 and 5.33168. Other different types of starch are also present in the sample but not as significant as the cellulose and polysaccharide. The surface morphology as scanned via Field Emission Scanning Electron Microscopy (FESEM) is rough with the fibers twisted indicating that the bonds between the molecules are strong and stable. The strong hydrogen bonds in the structure are associated with the structure of molecular cellulose. Surface area of the CMC is quantified utilizing a pore size analyser. The surface area of the banana peel CMC is sufficiently large (0.0558 ± 0.0699 m$^2$/g) enabling it to interact with other molecules to dissolve easily in solvents such as water. The Pore volumes and pore sizes of CMC will show that the size is sufficiently large to facilitate the adsorption and desorption process where 10 Å is recommended to be sufficient for the process to progress [12].

The average DS value of CMC calculated from Equation (3) and (4) is 0.62, above the recommended limit of 0.5 [3], and is regarded to be sufficient for solubility. Table 2 summarizes the spectrum of elements by weight % and atomic %. The element most found in the biopolymer is carbon (C) and
oxygen (O) which is 49.60 and 43.23 by weight %, respectively indicating that the cellulose occupies 92.83% of the biopolymer which is the most important element needed to synthesize a good drag reduction agent [13].

3.2. Drag Reduction Assessment
The centrifugal force due to the rotation of the inner cylinder of a double concentric cylinder leads to the destabilization of the flow field. The point at which the streamlines ceases to be circular for a Newtonian liquid and at which the flow field presents Taylor instabilities can be found by [14] and it should occur at a critical Reynolds Number defined by:

\[
R_e = \frac{\Omega R_m (\Delta R)}{\mu} > \left( \frac{R_m}{\Delta R} \right)^{0.5} \tag{5}
\]

where \(R_m = R_3\) and \(\Delta R = R_4 - R_3\). Prior to any further measurements of drag reduction, fresh tap water sample is tested under the rheometer as a reference.

3.3. Effect of Reaction Temperature
The 100ppm biopolymers produced at different reaction temperatures of 50°C, 55°C and 60°C for 240 minutes using 40% NaOH are mixed with UTP tap water. All the samples are left overnight after mixing for de-aeration and subsequently tested using the rheometer on Day 1, Day 3, Day 7 and Day 14. The results are summarized in figures 1, 2 and 3.
The graphs show that the drag reduces when the biopolymer is mixed with water. Sample 1 gives the best drag reduction. This shows that banana peel synthesized at 50°C with constant reaction time and concentration of NaOH yield higher Carboxymethylcellulose as indicated by the highest drag reduction performance followed by reaction at the temperature of 55°C and finally at 60°C. Temperature of 50°C is hence the optimum temperature to convert the cellulose to CMC above which the CMC structure is thought to degrade under such high temperatures. Over the duration of 14 days, the drag reduction percentage reduced by as much as 6.64%, calculated at 300 rad/s, indicating that the sample degrades over time.

3.4. Effect of Reaction Time

With the reaction temperature kept constant at 50°C and concentration of sodium hydroxide remained at 20% during synthesis, the reaction time is varied at 60, 150 and 240 min. All the samples are mixed at 100 ppm and left overnight for de-aeration and subsequently tested on Day 1, Day 3, Day 7 and Day 14. Figures 4, 5 and 6 summarize the findings.

It is observed that a reaction time of 60 minutes produced CMC with progressively good drag reduction capability up until day 7 beyond which the drag reduction ability reduces. However, when the sample is subjected to reaction times of 150 and 240 minutes the CMC produced exhibit reduction in drag reduction capability after day 3. Such performance is thought to be due to the prolonged reaction time the sample is exposed to during synthesis. The reaction time will affect the swell-ability of the cellulose.
Though swell-ability provides a better environment for carboxymethylation reaction even higher reaction time may significantly cause degradation of the cellulose chain and the CMC structure. The degree of substitution (DS) of the Carboxymethyl group increases with the increase of reaction time.

3.5. Effect of NaOH Concentration

The reaction time is maintained at 150 minutes with the reaction temperature set at 55°C. The concentrations of NaOH used for the synthesis are 20w/w%, 40w/w% and 60w/w% respectively. All the samples are mixed at 100ppm and left overnight for de-aeration and subsequently tested on Day 1, Day 3, Day 7 and Day 14. Figures 7, 8 and 9 summarize the findings.

![Figure 7](image1.png)

**Figure 7.** Torque profile for water and 100 ppm of biopolymer solution synthesized with 20% w/w NaOH concentration.

![Figure 8](image2.png)

**Figure 8.** Torque profile for water and 100 ppm of biopolymer solution synthesized with 40% w/w NaOH concentration.

![Figure 9](image3.png)

**Figure 9.** Torque profile for water and 100 ppm of biopolymer solution synthesized with 60% w/w NaOH concentration.

When determining the production of CMC, the concentration of NaOH plays a significant role. The proportion of NaOH must be optimum to obtain a high value of degree of substitution. The increase of NaOH concentrations affects the percentage yield of CMC, which is indirectly linked to the drag reduction performance. The reduced yield is due to the side reaction which takes place and results in the formation of sodium glycolate from the monochloroacetic acid. A side reaction is a carboxymethylation process which converts the monochloroacetate to sodium glycolate. The monochloroacetic acid molecules react with the NaOH leading to the destruction of cellulose chains or CMC polymer [15], [1]. From the figures, the yield of CMC is highest at 40% of NaOH where the drag reduction is progressively increasing from day 1. This finding could be explained by considering the carboxymethylation procedure described above, where two competitive reactions took place simultaneously; the first...
reaction to produce the CMC and the second reaction resulting in a by-product. This result shows that the first reaction prevails over the second reaction up to a NaOH concentration of 40%, beyond which the sodium glycolate is formed instead. 20% NaOH concentration is considered insufficient for the first reaction to be completed. Polymer degradation could also take place at high concentrations of NaOH. Similar observations are documented in maize starch [16], corn starch [17], sago waste [18], potato starch [19] and pigeon pea starch [20]. The nature and composition of organic solvents used as reaction media plays an important part in the structural transformation of cellulose during alkalization. The nature of biopolymer affects the biodegradability as the isopropyl alcohol having dielectric constant is a bad solvent for sodium hydroxide and it favors higher concentration of NaOH in the vicinity of cellulose, giving rise to substantial change of polymorphism.

4. Conclusion

For the first time, Carboxymethylcellulose (CMC) is produced from the Cavendish banana peel using the Carboxymethylation process. Twenty-seven samples are synthesized to cover all the different parameters. Material characterization is performed on the banana peel CMC via X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Pore Size Analyzer (BET). The characterization analysis shows that the cellulose is the strongest component in the sample occupying 92.83% of the biopolymer. The Double concentric cylinder (DCC) geometry in the stress-controlled rheometer is utilized in this study to assess the drag reduction. The drag reduction performance is thought to be linked to the amount and quality of the CMC produced under various parameters. Varying the reaction temperature during synthesis, the biopolymer synthesized at the lowest chosen reaction temperature of 50°C works best at drag reduction. The drag reduction performance starts to decrease when it is synthesized at higher temperatures due to degradation of CMC. Another synthesis parameter varied is the reaction time. The experimental results imply that prolonged reaction time results in the degradation of CMC structure and hence decreases the drag reduction capability. When the NaOH concentration is varied, the solution with an optimum NaOH concentration of 40% utilized during synthesis gave the best drag reduction capability. During synthesis, two reactions are anticipated to have taken place in producing the CMC; the first reaction involves cellulose hydroxyl with monochloroacetic acid in the presence of NaOH to produce CMC and the second reaction results in the conversion of monochloroacetate to sodium glycolate as a by-product. This study implies that sodium glycolate might have formed at higher NaOH concentrations. The findings presented in this paper prove that green Cavendish banana peel CMC has a great potential at drag reduction when synthesized at the right conditions.

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