Abstract- The viscosity and fluidity of a starch solution with a water-starch ratio of 2.0w/w was studied during gelatinisation under strong alkali conditions, in a Co-axial cylinder viscometer for 17g/dm³ - 23g/dm³ concentrations of NaOH solution.

The degree of gelatinization was defined in terms of viscosity and the experimental data fit to eleven rate equations based on the mechanism of the unreacted-core model.

The model for Product layer diffusion plus Chemical reaction control (F) gave the best fit (0.9930 ≤ R² ≤ 0.9999) to the experimental data at all sodium hydroxide concentrations studied, with the Product layer diffusion control step dominating at low sodium hydroxide concentrations while the Chemical reaction control step dominated at high sodium hydroxide concentrations.

This model can serve as a guide for obtaining specific concentrations of sodium hydroxide to be used for production of an adhesive with a pre-determined viscosity or to develop a robust model for optimising the process of producing adhesives from starch.

Keywords- starch, gelatinisation, viscosity, fluidity, rheological, equilibrium

I. INTRODUCTION

Starch is one of the most common substances existing in nature and is the major basic constituent of the average diet. The most important practical property of starch is its ability to undergo hydration, irreversible swelling, crystallite melting, loss of birefringence and solubilisation under the influence of heat and/or certain chemical in an aqueous medium to give starch paste. This process is called gelatinization.

The chemical gelatinization of starch-under strong alkali conditions-is the basic industrial reaction in the conversion of starch to adhesives (glue)(Leach, 1965; Austin, 1985; Halley & Sopade, 2004;www.cerestar.com, 2004).

This demand for starch base glues notwithstanding, much less is known about alkali gelatinization-compared to thermal gelatinization-and especially no kinetic approach has appeared in open literature (Yamamoto et.al. 2005).

In order to develop the kinetics of starch gelatinization using the rheological approach, one must properly define a physical (measurable) quantity that is related to a degree of gelatinization and must measure its time dependence under isothermal conditions.

II. THEORETICAL PRINCIPLES

A. Model Development

Starch gelatinization under strong alkali conditions is a heterogeneous (fluid-particle) reaction in which a liquid (water) reacts with a solid (starch) to produce an adhesive paste, in the presence of an alkali (sodium hydroxide). Sodium hydroxide weakens the micellar network within the starch granules by disrupting hydrogen bonds. This permits further hydration and irreversible granule swelling with paste viscosity rising rapidly to a peak value (Leach, 1965).

Such reactions are represented as:

A (fluid) +bB (solid) → Fluid Products

(1) → Solid Products

(2) → Fluid and Solid Products

(3)

In the first case, the solid particle shrinks in size during the reaction. This is usually the case when a pure solid is used as reactant or a flaking product is formed.

In the last two cases, the solid particle remains unchanged in size during the reaction. This is the case when an impure solid is used as reactant or a firm solid product is formed.

Yagi and Kunii (1955) developed a model called the unreacted-core model, which has gained a wide acceptability in modeling fluid-particle reactions. They visualised that the reaction first occurs at the outer skin of the particle. The zone of reaction then moves into the solid and may leave behind completely converted material or inert solid. There exists at any time an unreacted core of material, which shrinks in size during the reaction.

For an irreversible heterogeneous reaction as gelatinisation, the model visualized three steps occurring in succession, any of which could be rate controlling.
STEP 1: Diffusion of the reacting fluid through film surrounding the solid particle, to the surface of the solid.

STEP 2: Diffusion of the reacting fluid through the product layer to the surface of the unreacted core.

STEP 3: Chemical reaction of the reacting fluid with the solid at this surface.

For most cases where the particle shrinks in size, the second step does not play any role. This step cannot be ignored for gelatinisation because the viscous paste formed is closely attached to the unreacted solid and could offer resistance to diffusion.

Assumptions:
- Starch particles are spherical in shape.
- Interaction between starch particles is negligible.
- The degree of gelatinization is equivalent to conversion.

The following equations relating time (t), time for complete conversion (T) and conversion (x) at any time, have been developed for different rate controlling steps, based on a spherical particle:

1. Film Diffusion Controls (Stokes regime):
   \[ t / \tau = 1 - (1 - x)^{2/3} \]  

2. Film Diffusion (Non-stokes regime):
   \[ t / \tau = 1 - (1 - x)^{1/2} \]  

3. Product Layer Diffusion Controls:
   \[ t / \tau = 1 - 3(1 - x)^{2/3} + 2(1 - x) \]  

4. Chemical Reaction Controls:
   \[ t / \tau = 1 - (1 - x)^{1/3} \]  

The relative importance of the Fluid film, Product layer and Chemical reaction steps will vary as conversion progresses. In general, then, it may not be reasonable to consider that just one step controls throughout the reaction. To account for simultaneous action of these resistances, it can be shown that the time to reach any stage of conversion is the sum of times needed if each resistance acted alone (Levenspiel, 2006).

\[ t_{total} = t_{film \ alone} + t_{product\ layer\ alone} + t_{chemical\ reaction\ alone} \]  

\[ \tau_{total} = \tau_{film\ alone} + \tau_{product\ layer\ alone} + \tau_{chemical\ reaction\ alone} \]  

Thus we can develop models where two steps or three steps are rate-controlling.

### III. MODIFICATION OF MODELS

One experimental observation from starch gelatinization under strong alkali conditions, which is also in agreement with literature, is that there is always a time lag between the contacting of reactants and any observable reaction. This is the time it takes for the starch particles to adsorb the required amount of sodium hydroxide to break its hydrogen bonds and make it susceptible to gelatinization (Leach, 1965; Mangels and Bailey, 1995).

On modification of the original equations by including the lag or delay time (td), we have:

1. Film Diffusion Controls (Stokes regime):
   \[ (t - t_d) = \tau (1 - (1 - x)^{2/3}) \]  

2. Film Diffusion Controls (Non-stokes regime):
   \[ (t - t_d) = \tau (1 - (1 - x)^{1/2}) \]  

3. Product Layer Diffusion Controls:
   \[ (t - t_d) = \tau (1 - 3(1 - x)^{2/3} + 2(1 - x)) \]  

4. Chemical Reaction Controls:
   \[ (t - t_d) = \tau_c (1 - (1 - x)^{1/3}) \]  

These four rate equations (eq.10 - eq.13) can be combined with eq.8 to account for situations when more than one step is rate-controlling, thus:

### One-Step Controls

- **A1** Diffusion through fluid film controls (stokes regime)
  \[ (t - t_{1\Al}) = \tau_{Al}(1 - (1 - x)^{2/3}) \]

- **A2** Diffusion through fluid film controls (non-stokes regime)
  \[ (t - t_{2\Al}) = \tau_{Al}(1 - (1 - x)^{1/2}) \]

- **B** Diffusion through Product layer controls
  \[ (t - t_{B}) = \tau_{p}(1 - 3(1 - x)^{2/3} + 2(1 - x)) \]

- **C** Chemical reaction controls
  \[ (t - t_{C}) = \tau_{c}(1 - (1 - x)^{1/3}) \]

### Two-Step Controls

- **D1** Film diffusion plus Product layer controls (stokes regime)
  \[ (t - t_{1\Al}) = \tau_{Al}(1 - (1 - x)^{2/3}) + \tau_p(1 - 3(1 - x)^{2/3} + 2(1 - x)) \]

- **D2** Film diffusion plus Product layer controls (non-stokes regime)
  \[ (t - t_{2\Al}) = \tau_{Al}(1 - (1 - x)^{1/2}) + \tau_p(1 - 3(1 - x)^{2/3} + 2(1 - x)) \]

- **E1** Film diffusion plus Chemical reaction controls (stokes regime)
  \[ (t - t_{1\Ac}) = \tau_{Al}(1 - (1 - x)^{2/3}) + \tau_{c}(1 - (1 - x)^{1/3}) \]

- **E2** Film diffusion plus Chemical reaction controls (non-stokes regime)
  \[ (t - t_{2\Ac}) = \tau_{Al}(1 - (1 - x)^{1/2}) + \tau_{c}(1 - (1 - x)^{1/3}) \]

- **F** Product layer diffusion plus Chemical reaction controls
  \[ (t - t_{Ac}) = \tau_p(1 - 3(1 - x)^{2/3} + 2(1 - x)) + \tau_{c}(1 - (1 - x)^{1/3}) \]
Three-Step Controls
G1 Film diffusion plus Product layer plus Chemical reaction controls (stokes regime)
\[(t-t_{ac}) = \tau_1 (1 - (1 - x)^{2/3}) + \tau_2 (1-3(1-x)^{2/3}) + 2(1-x) + \tau_c (1 - (1-x)^{3/2})\]  \hspace{1cm} (23)
G2 Film diffusion plus Product layer plus Reaction controls (non-stokes regime)
\[(t-t_{ac}) = \tau_{c2} (1 - (1 - x)^{3/2}) + \tau_{c1}(1-3(1-x)^{2/3}) + 2(1-x) + \tau_c (1 - (1-x)^{3/2})\]  \hspace{1cm} (24)
These rate equations (eq. 14 – eq. 24) can be used with the MATLAB curve fitting toolbox without modification, for analysis of experimental data.

IV. MATERIALS AND METHODS
A. Raw Materials:
Distilled water, Cassava starch and Sodium hydroxide (NaOH).

B. Equipments and Apparatus:
Glass beakers (250 cm3), Measuring cylinders, Stopwatch, Conical flask, Temperature sensors, Electronic-weighing balance, Glass rod stirrer, Sieve cloth, Knife, Grating device, Co-axial cylinder viscometer and Water bath.

C. Starch Gelatinization Study
(i) 50grams of the dry starch powder was weighed out and dispersed in 100 cm3 of distilled water, to obtain dispersion with a water to starch ratio of 2:1(Freitas et. al., 2002).
(ii) 100 cm3 of starch dispersion prepared in (i) above was measured into a metallic cylindrical vessel – originally a component of the coaxial cylinder viscometer – and 100 cm3 of sodium hydroxide solution was added to it. The metallic cylindrical vessel served as the reactor.
(iii) The metallic cylindrical vessel (laboratory reactor) was then incorporated into the coaxial cylinder viscometer set up. The coaxial cylinder viscometer was set at a specified shear rate of 1 rpm and switched on.
(iv) The corresponding shear stress was read off the dial of the viscometer at intervals of ten seconds, with the rate of agitation kept constant throughout the experiment and in subsequent experiments.
(v) The dial reading (shear stress) was converted to standard viscosity units using factors provided by the manufacturers of the coaxial cylinder viscometer (Nelson, 1990; Chandler Engineering, 2004). Thus, viscosity = F* (Dial reading). The inverse of the viscosity was recorded as the fluidity.
(vi) The experimental procedure was repeated for all sodium hydroxide concentrations.

V. RESULTS, DATA ANALYSIS AND DISCUSSION
Based on the work of Osoka et. al. (2008) the equilibrium fluidity was obtained by fitting the fluidity-time curve to the model, \[F = F_e \exp(Kt^2),\] where \(n < 0\) and \(F_e\) the equilibrium fluidity (value of Fluidity (F) as time (t) tends to infinity) and equilibrium viscosity obtained as the inverse of the equilibrium fluidity.

The degree of gelatinization (conversion) was defined in terms of viscosity as \[x = \frac{\mu_0 - \mu}{\mu_0 - \mu_f} \]

<p>| Table 1. Numerical fit results for 17g/dm³ NaOH Concentration |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Model</th>
<th>(\tau_f) (secs)</th>
<th>(\tau_f) (secs)</th>
<th>(\tau_f) (secs)</th>
<th>(\tau_f) (secs)</th>
<th>R²</th>
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<tr>
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<p>| Table 2. Numerical fit results for 18g/dm³ NaOH Concentration |
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<th>(\tau_f) (secs)</th>
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<tr>
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<td>10.42</td>
<td>575.4</td>
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<td>219.7</td>
<td>564.1</td>
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<tr>
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<td>243</td>
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<p>| Table 3. Numerical fit results for 19g/dm³ NaOH Concentration |
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A. One-Step Control Models

The fit results show that the model for Film diffusion control under stokes regime and non-stokes regime (A1 and A2) do not fit the experimental data except at high sodium hydroxide concentrations of 22g/dm$^3$ and 23g/dm$^3$. For other concentrations of sodium hydroxide, the models under-predict the experimental data at low conversions ($x < 0.4$) and over-predicts it at higher conversions.

The fit results of the model for Product layer diffusion control (B) shows that it gives a better fit when lower concentrations of sodium hydroxide were used. It also fits the data at higher values of conversion, especially $x > 0.6$, but performs poorly for high concentrations of sodium hydroxide (22g/dm$^3$ and 23g/dm$^3$) and at very low conversions ($x < 0.25$) where it over-predicts the experimental data.

The model for Chemical reaction control (C) does not fit the data except for sodium hydroxide concentrations of 18g/dm$^3$, 22g/dm$^3$ and 23g/dm$^3$. It also under-predicts the data at low conversions ($x < 0.4$), for most sodium hydroxide concentrations. Nevertheless, it gives a better fit than all other one-step control models.

B. Two-Step Control Models

The model for Film diffusion (stokes regime) plus Product layer diffusion control (D1) gave a good numerical fit (0.9924 ≤ $R^2$ ≤ 0.9999) for the experimental data at all sodium hydroxide concentrations, but the graphical fit results show that it performs poorly at very low conversions. The numerical fit results also show that the Product layer diffusion step dominates for most sodium hydroxide concentrations, as can be seen from the values of time for complete conversion.

The fit results for Film diffusion (non-stokes regime) plus Product layer diffusion control (D2) are similar to D1 with a good numerical fit (0.9926 ≤ $R^2$ ≤ 0.9999) for all sodium hydroxide concentrations, with the Product layer diffusion step dominating.

The graphical fits for Film diffusion (stokes regime) plus Chemical reaction control (E1) model and Film diffusion (non-stokes regime) plus Chemical reaction control (E2) model are similar. They under-predict the experimental data at low conversions ($x < 0.4$) and give numerical fits with $R^2 > 0.99$ for 18g/dm$^3$, 22g/dm$^3$ and 23g/dm$^3$ sodium hydroxide concentrations. The Chemical reaction control step plays the dominant role for most sodium hydroxide concentrations.

The model for Product layer diffusion plus Chemical reaction control (F) gave a good numerical fit (0.9930 ≤ $R^2$ ≤ 0.9999) for the experimental data at all sodium hydroxide concentrations. The Product layer diffusion control step dominates at low sodium hydroxide concentrations while the
Chemical reaction control step dominates at high sodium hydroxide concentrations.

For most sodium hydroxide concentrations, the Two-step control models are an improvement on the One-step control models.

C. Three-Step control Models

The model for Film diffusion (stokes regime) plus Product layer diffusion plus Chemical reaction control (G1) and Film diffusion (non-stokes regime) plus Product layer diffusion plus Chemical reaction control (G2) have similar graphical and numerical fit results ($0.9930 \leq R^2 \leq 0.9999$) for all concentrations of sodium hydroxide. This means that the fit results were not improved.

Two steps at most were rate controlling for all sodium hydroxide concentrations, with the third step having a value of time for complete conversion approximately equal to zero.

Product layer diffusion and Chemical reaction steps controlled the rate for most concentrations of sodium hydroxide. The delay time ($t_d$) obtained for the Three-Step control models and its fits matched with those of Product layer diffusion plus Chemical reaction control (F) model for most sodium hydroxide concentrations. It is therefore not necessary to model for Three-Step control.

The model with the best fits for all conversions is that of Product layer diffusion plus Chemical reaction control (F), followed by D2 and D1 respectively. It can be observed that these three rate equations have the Product layer diffusion step in common.

The performance of most of the models at low conversion makes it imperative to consider the experimental data in two phases, at low conversion ($x < 0.4$) and at high conversion ($x \geq 0.4$).

VI. CONCLUSION

Starch gelatinization under strong alkali conditions is a heterogeneous (fluid-particle) reaction based on the mechanism of the unreacted-core model. The individual granules adsorb alkali and gelatinise when the amount of adsorbed alkali exceeds a certain threshold concentration (Leach, 1965; Mangels and Bailey, 1993).

The model for Product layer diffusion plus Chemical reaction control (F) gave the best fit ($0.9930 \leq R^2 \leq 0.9999$) for the experimental data at all sodium hydroxide concentrations with the Product layer diffusion control step dominating at low sodium hydroxide concentrations while the Chemical reaction control step dominates at high sodium hydroxide concentrations.

The performance of most of the models at low conversion though, makes it imperative to consider the experimental data in two phases, at low conversion ($x < 0.4$) and at high conversion ($x \geq 0.4$). (see figure 1 at the next page)

REFERENCES

Fig. 1: Sample Graphical fit results of conversion (x) vs. time (t) for all models using 20g/dm$^3$ NaOH concentration.