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Effect of Sodium Hydroxide Concentration on Kinetic Parameters during Gelatinisation

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Abstract
Viscosity and fluidity profiles of a starch solution with a water-starch ratio of 2.0w/w during gelatinisation under strong alkali conditions, in a Co-axial cylinder viscometer for 17g/dm^3 - 23g/dm^3 concentrations of NaOH solution was studied. This work models the variation of the equilibrium viscosity, equilibrium fluidity, gelatinization rate, gelatinization constant and delay time with Sodium hydroxide concentration. The equilibrium fluidity and delay time were fit to third and second order polynomials respectively, while the gelatinization rate and equilibrium viscosity fit to first and second order Gaussian models respectively and the gelatinization constant to a rational function with R^2 > 0.99 in all cases. These parameters and models can be used to simulate starch gelatinization beyond the range of experimental data.

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

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 gelatinisation.

The chemical gelatinisation 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).

The rate of starch gelatinisation under strong alkali conditions can be studied rheologically, with the degree of gelatinisation defined in terms of viscosity and modeled based on the mechanism of the unreacted-core model. Two steps at most are rate controlling (Yagi and Kunii, 1955; Yamamoto et al, 2005; Levenspiel, 2006; Osoka et al. 2008; Osoka and Njiribeako, 2009).

Most kinetics parameters during starch gelatinisation under strong alkali conditions vary with the concentration of alkali, hence the need to model these parameters for the purpose of data interpolation and extrapolation beyond available experimental data.

These kinetic parameters include: equilibrium fluidity (Pa.s)$^{-1}$, equilibrium viscosity (Pa.s), gelatinisation rate (no units), gelatinisation constant (no units) and delay (lag) time (secs).

Data Analysis
The following data are available from previous work:

Table 1: Parameters of the Fluidity-time curve ($F=F_e\exp(Kt^n)$) and equilibrium Viscosity

NaOH Conc. (g/dm^3)	F_e (Pa.s)$^{-1}$	K	n	R^2	RMSE	SSE	μ_e(Pa.s)
17	0.02799	7.584e+7	-3.263	0.9995	9.33e-4	2.176e-5	35.7270
18	0.02240	1.595e+7	-3.069	0.9991	2.141e-3	1.467e-4	44.6429
19	0.01708	9.2e+5	-2.666	0.9999	3.227e-4	2.915e-6	58.5480
20	0.01196	1.7721e+4	-1.970	0.9992	5.199e-4	1.054e-5	83.6120
21	0.008742	3088	-1.690	0.9999	1.921e-4	6.271e-7	114.3963
22	0.005515	90.75	-1.138	0.9996	9.528e-4	2.724e-6	181.3237
23	0.004965	12.95	-0.7073	0.9997	5.141e-4	5.285e-7	201.4099

Source: Osoka et al (2008)

Table 2: Delay (lag) time for 17g/dm^3-23g/dm^3 NaOH Concentrations

NaOH Conc. (g/dm^3)	17	18	19	20	21	22	23
Delay time, t_d (secs)	186.7	149.4	107.7	82.42	54.49	15.81	5.281

Source: Osoka and Njiribeako (2009)

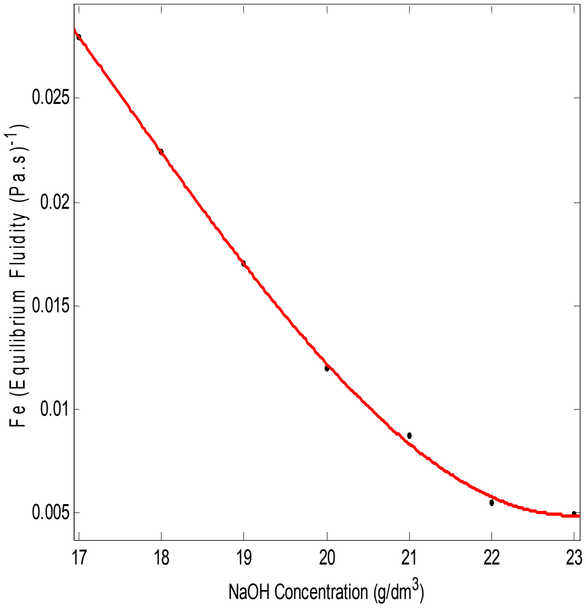

Fig. 1: Equilibrium Fluidity (Pa.s)$^{-1}$ against NaOH Concentration (g/dm^3)

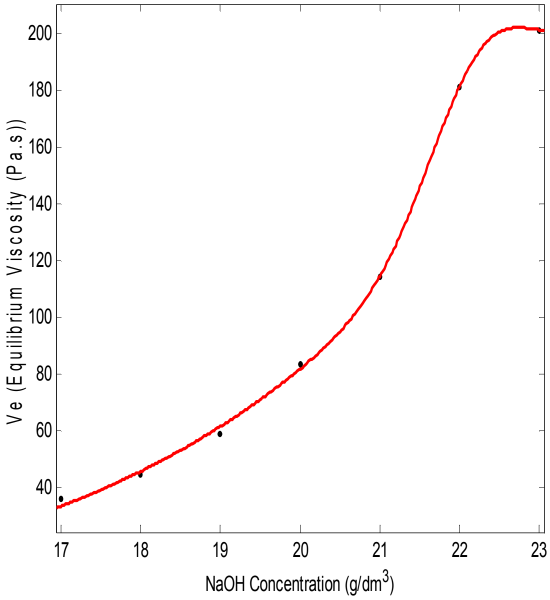

Fig. 2: Equilibrium Viscosity (Pa.s) against NaOH Concentration (g/dm^3)

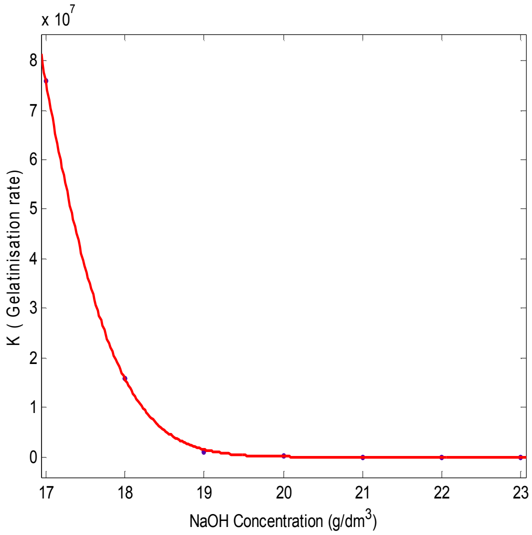

Fig. 3: Delay Time, t_d (secs) vs. NaOH Concentration (g/dm^3)

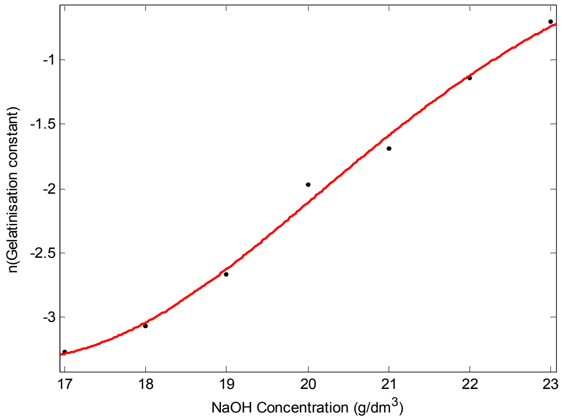

Fig. 4: Gelatinisation constant (n) vs. NaOH Concentration (g/dm^3)

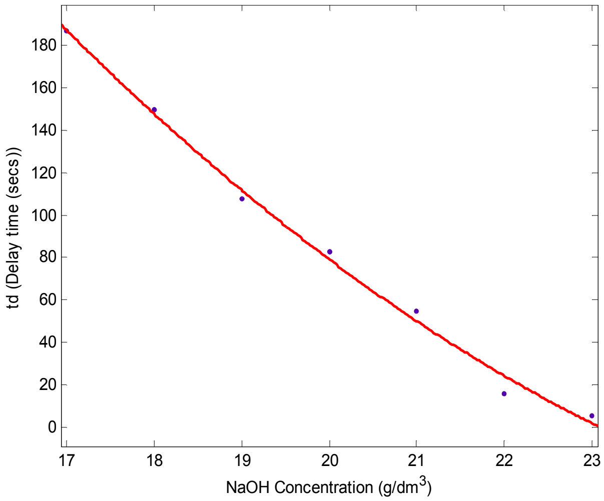

Fig. 5: Delay (lag) time (secs) vs. NaOH Concentration (g/dm^3)

Model Equations

Equilibrium Fluidity: $F_e = p_1x^3 + p_2x^2 + p_3x + p_4$ (1)

Equilibrium Viscosity: $\mu_e = a_1 \exp(-((x-b_1)/c_1)^2)$ (2)

Gelatinisation Rate:

$$K=a_1\exp(-((x-b_1)/c_1)^2)+a_2\exp(-((x-b_2)/c_2)^2) \quad (3)$$

Gelatinization Constant: $n = \dfrac{p_1x + p_2}{x^2 + q_1x + q_2}$ (4)

Delay (lag) Time: $t_d = p_1x^2 + p_2x + p_3$ (5)

For all cases, x represents Sodium hydroxide concentration in g/dm^3

Table 3: Numerical fit result and Parameters for Polynomial Models

Parameter	P_1	P_2	P_3	P_4	q_1	q_2	R^2
F_e	6.106e-5	-0.003193	0.05007	-0.2003	-	-	0.9993
n	12.64	-334.3	-	-	-36.26	363.9	0.9939
t_d	1.71	-99.29	1381	-	-	-	0.9951

Table 4: Numerical fit result and Parameters for Gaussian Models

Parameter	a_1	b_1	c_1	a_2	b_2	c_2	R^2
μ_e	1004	38.24	11.51	48.11	22.28	0.9554	0.9993
K	1.456e8	15.81	1.467	-	-	-	0.9999

DISCUSSION

Figure 1 shows that the equilibrium fluidity decreases exponentially and tends to a finite value as sodium hydroxide concentration is increased from $17g/dm^3$ to $23g/dm^3$ and the profile fits to a third order polynomial with $R^2 > 0.99$.

Figure 2 shows that the equilibrium viscosity increases slowly with increase in sodium hydroxide concentration up to a concentration of $21g/dm^3$, producing a concave profile. Between sodium hydroxide concentrations of $21g/dm^3$ and $23g/dm^3$ it increases very rapidly and forms a convex profile that tends to approach a finite value at higher concentrations. This profile fits to a first order Gaussian model with $R^2 > 0.99$.

This would mean that higher concentrations of sodium hydroxide would not increase the equilibrium viscosity. The equilibrium viscosity will have a maximum value for each water-starch ratio chosen.

Figure 3 shows that the gelatinisation rate decreases exponentially and tends to a finite value at high concentrations of sodium hydroxide while figure 4 shows that the gelatinisation constant increases almost linearly for all concentrations of sodium hydroxide. The gelatinization rate fits to a second order Gaussian function and the gelatinization constant fits to a linear-to-quadratic rational function.

Figure 5 shows that the lag (delay) time decreases almost linearly, almost at a constant rate, with sodium hydroxide concentration up to a concentration of $22g/dm^3$. Beyond this concentration, the rate of decrease of lag time with sodium hydroxide concentration reduced drastically as the lag (delay) time gets close to zero. Thus starch gelatinization for high concentrations of alkali will be spontaneous.

The profile fits well to a quadratic model with $R^2 > 0.99$.

CONCLUSION

The five kinetic parameters of starch gelatinization under strong alkali conditions are all functions of alkali concentration.

The equilibrium fluidity and delay time gave good fit to third and second order polynomials respectively, while the gelatinisation rate and equilibrium viscosity gave good fits to first and second order Gaussian models respectively and the gelatinization constant to a rational function with $R^2 > 0.99$ in all cases.

These parameters and models can be used to simulate starch gelatinization beyond the range of experimental data, especially using the equation: $F = F_e \exp(Kt^n)$

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