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Jet-cooked papermaking starches studied using ^1H NMR-relaxometry and viscometry

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Abstract: Two wet-end starches (potato and barley), one surface sizing starch (barley) and one coating binder starch (barley) were jet-cooked. Samples were collected and stored at 90, 60 and 40 °C. ^1H NMR-relaxometry and viscometry were used to monitor the jet-cooked solutions as they cooled to room temperature. Samples stored at different temperatures were also monitored using ^1H NMR-relaxometry and viscometry. A sediment formed into the surface sizing and coating binder starches stored at 90 °C. The sediment and supernatant were separated and collected, and measured using ^1H NMR-relaxometry. The T_2 relaxation rates of jet-cooked starches showed significant differences between potato and barley starches, as had also been examined in previous studies. The NMR method was also sensitive to differences in solids content and chemical modification (degree of cationization, degree of oxidation and molecular weight). The cooking temperature, cooking speed and viscosity did not influence T_2 relaxation rates. The sediment separated from the surface sizing and coating binder starches held at 90 °C had a significantly higher relaxation rate than the supernatant, indicating that the sediment contained a high amount of retrograded starch.

Keywords: ^1H NMR-relaxometry; jet-cooking; paper chemicals; starch; viscometry.

Introduction

In papermaking, it is common knowledge that starch should be well-cooked, i.e. fully gelatinized, to enable it to bind properly with cellulose fibers. This is usually

achieved by using a jet-cooker, which utilizes steam to generate heat and shear forces to gelatinize a starch slurry (BeMiller and Maurer 2005, Neimo 1999).

Starch has been widely studied in the context of food and papermaking, and there are many books and review articles explaining the structure of starch and the mechanisms behind gelatinization and retrogradation (BeMiller and Maurer 2005, Lehtinen 2000, Maurer 2007, Wang et al. 2015). Starches can be characterized in multiple ways, such as viscosity, calorimetry, NMR-relaxometry, NMR-spectroscopy, X-ray diffraction, turbidity and iodine staining (Wang et al. 2015).

^1H NMR-relaxometry, i.e. time-domain ^1H NMR, is a useful tool for measuring changes occurring in a system such as a starch slurry because the NMR relaxation signal is directly related to the structure of the starch and its interactions with water. Temperature, solids content, viscosity, gelatinization and retrogradation all have an effect on the protons in the sample and thus impart a change to the NMR signal (Nivelle et al. 2019, Zhu 2017). In addition, NMR measurements can be made continuously, quickly and non-destructively. On the other hand, because the NMR signal is influenced by so many factors, its interpretation can be difficult. Concisely put, the following proton populations are the ones that contribute to the NMR-relaxometric signal: protons of the starch macromolecules, intra-granular water protons, extra-granular water protons in high interaction with starch, and extra-granular water protons in low interaction with starch. The macromolecule protons can be detected with a free induction decay (FID) pulse sequence, and the other protons can be detected with a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence (Kovrlja and Rondeau-Mouro 2017).

When one reads articles about food starch studies, it is important to notice that often in them the solids content of the starch is much higher than in papermaking, which has a major influence on the mechanisms of the water-starch system. In addition, food starches are often native starches, whereas papermaking starches are typically chemically modified, which influences their behavior (e.g. viscosity) in many ways (BeMiller and Maurer 2005).

The goal of this study was to examine the effect of jet-cooking on chemically modified potato and barley

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starches. Potato starch and barley starches were chosen because they represent two different starch categories, tuber and cereal. Potato starch is generally easier to cook, whereas cereal starches, such as barley and wheat, are more difficult to prepare (Hermansson and Svegmärk 1996). ^1H NMR-relaxometry and viscometry were chosen as the measurement tools because they both have been widely used for starch characterization (BeMiller and Maurer 2005, Bosmans et al. 2012).

Some studies have previously been undertaken regarding jet-cooked starches (Fanta et al. 1999, 2002, Ferng et al. 2011). However, to the best of our knowledge, jet-cooked starches have not been previously studied using ^1H NMR-relaxometry in combination with viscometry.

In this study, the results are presented as relaxation rates (R_2), which is the inverse of spin-spin relaxation time T_2 . As the mobility of protons increases, the R_2 value decreases, and vice versa. The most important factors affecting the relaxation rate are the following:

- 1) Due to the Arrhenius effect, the mobility of protons increases when temperature increases, which decreases R_2 (Nivelle et al. 2019).
- 2) As viscosity increases, the mobility of protons decreases, which increases R_2 (Nivelle et al. 2019).
- 3) As the starch becomes gelatinized, the mobility of protons increases, which decreases R_2 (Wang et al. 2015).
- 4) As the starch retrogrades, the mobility of protons decreases, which increases R_2 (Lionetto et al. 2005).

Materials and methods

Materials

The studied starches were provided by Chemigate Oy, Finland. Raisamyl 70021 and Raisamyl 80051 are cationized, high molecular weight (MW) wet-end starches that have a degree of substitution (DS) of 0.042 and 0.044, respectively. Raisamyl 23151 is a cationized and oxidized surface sizing starch with a DS of 0.018 and a medium MW of approximately a few million Da. Raisamyl 01151 is an oxidized coating binder starch with a smaller MW of approximately a million Da. Raisamyl 70021 is a potato starch, whereas the other starches are barley starches. The starch slurry was prepared into cold (18 °C) tap water.

NMR-equipment

The ^1H NMR-relaxometry measurements were performed using a TD-NMR (time-domain NMR) system (Resonance

systems ltd., 2019). The ^1H resonance frequency of the system was 26 MHz, and the temperature of the magnet was 30 °C. Spin-spin relaxation rates R_2 were measured by applying the CPMG pulse sequence (Abragam 1961). The echo time was 6 ms, and there were 600 180° pulses in the sequence. The relaxation delay was 6 s, and there were four scans. The durations of the 90° and 180° RF pulses were 7 μs and 16 μs , respectively.

For the measurements done immediately after jet-cooking, the system was modified for flowing samples, and the sample was automatically pumped through the system and measured. For the other measurements, the samples were simply measured in test tubes.

The instrument error of the NMR-equipment has been previously determined to be 0.72 % for black liquor samples (Nikolskaya et al. 2019).

Cooking and measurements

The jet-cooker used in this study is similar to the cookers used in paper mills; the starch slurry is continuously pumped into the system where it is mixed with steam, the heat and shear forces break down the starch structure, and the starch becomes gelatinized. Finally, the starch is pumped into a steam separator and a sample is collected. The cooking temperature is controlled by adjusting the amount of steam and backpressure. The cooking time is adjusted by changing the pump's speed. Due to the mixing of steam with the slurry, the solids content of the solution is reduced by approximately 25 % during cooking. Table 1 shows a summary of the studied starches' characteristics and the starch slurry solids contents before jet-cooking and during measurement.

After cooking, one sample was collected for NMR measurement, one for viscosity measurement and three samples for storage at 40, 60 and 90 °C. In addition, the surface sizing and coating binder starches were diluted with boiling water from a consistency of approximately 25 % to 13 % and from 35 % to 21 %, respectively, before sampling. The NMR and viscosity samples were allowed to cool to room temperature at approximately 1 °C/min. The NMR relaxation was measured on-line according to the following procedure:

- 1) A sample was continuously mixed in a container.
- 2) The sample was automatically pumped through the magnet system.
- 3) When a new sample was introduced to the system, the pump was stopped.

Table 1: Summary of the studied starches' characteristics and the starch slurry solids contents before jet-cooking and during measurement.

Starch	Origin	MW	Cationic	Oxidized	Application	Solids content (wt-%)	
						Cook	Measurement
70021	Potato	High	Yes (high)	No	Wet-end	5.0	4.2
80051	Barley	High	Yes (high)	No	Wet-end	5.0	3.6–3.7
23151	Barley	Medium	Yes (low)	Yes (low)	Surface sizing	25.0	12.4
01151	Barley	Small	No	Yes (high)	Coating binder	35.0	20.9

- 4) The CPMG signal was automatically measured and fitted using a mono-exponential function, and the R_2 value was solved.
- 5) The next sample was pumped.

Individual proton populations were not examined. Thus, the R_2 values presented in the Results and Discussion section are a combination of all the proton populations' relaxation rates visible with the CPMG signal. Viscosity was measured approximately every 10 °C using a Brookfield DV-II + Pro Extra Viscometer. The speed of the spindle was 100 rpm. From the samples stored at 40, 60 and 90 °C, NMR relaxation and viscosity were measured 1–2 times per day during the following 2 days. The NMR samples were stored in capped test tubes and were mixed lightly before measurement. The viscosity samples were mixed before measuring, and they were stored in capped containers to prevent evaporation.

The high-temperature retrogradation (HTR) sediment and supernatant were collected from a separate container, so as not to interfere with the NMR and viscosity measurements. The sediment and supernatant were separated by centrifuging at 5000 rpm for 5 min in a Hermle Z 200 A centrifuge. The HTR samples were then moved back into 90 °C for 30 minutes to prevent cooling from affecting the results, and finally their NMR relaxation was measured.

The relationship between starch solids content and NMR relaxation rate was determined by diluting the surface sizing barley starch solution with 27 °C water at the end of the NMR measurements done immediately after cooking, when the solution had cooled to 27 °C.

Results and discussion

NMR relaxation and viscosity after jet-cooking

Figure 1 shows the R_2 relaxation rates for the studied starches. The NMR curves representing the cooling of wet-end starches on the left are nearly identical to the curves

observed for cationic potato and barley wet-end starches in a previous study, in which batch cooking at 95 °C was studied at a similar consistency (Raunio et al. 2018). The points at approximately $T = 20$ °C and $R_2 = 0.8 \text{ s}^{-1}$ correspond to water only.

In Figure 1, the relaxation rate of jet-cooked wet-end potato starch remains very low (close to pure water) even at low temperatures. This is interpreted to mean that the starch has been fully gelatinized, and that it does not retrograde even at lower temperatures (60–30 °C). Wet-end barley starch behaves in a completely different manner; its R_2 value is quite low at a high temperature, but unlike in the case of potato starch, the R_2 quickly rises with decreasing temperature until about 50 °C. Interestingly, there is a small decrease in the lowest temperatures (40–30 °C).

This result can be interpreted in two ways. 1) The barley starch is fully gelatinized during jet-cooking, but it starts to retrograde anyway immediately afterward as temperature decreases, perhaps due to the lipids present in cereal starches forming complexes with amylose (Fanta et al. 1999), or simply due to the formation of an amylose network (BeMiller and Maurer 2005). 2) The barley starch has actually not been fully gelatinized, and because of this, it retrogrades quickly due to ghost particles left into the solution, which act as seed crystals (Smits et al. 2003). The second option seems implausible due to the high temperature and shear forces present in jet-cooking, which should break apart the starch structure very thoroughly.

Changing the cooking temperature from 120 °C to 140 °C or the cooking speed from 1.6 kg/min to 1.0 kg/min had a very small effect on the post-cooking R_2 values of the wet-end barley starch, which probably means that such a small difference in cooking temperature or time did not have a significant effect on the starch's gelatinization or retrogradation.

In the case of surface sizing and coating binder (barley) starches, the shapes of the NMR cooling curves are a bit different from the wet-end starches, and the R_2 values are larger. The higher R_2 values for these starches can partially be explained by the higher solids content, which

Figure 1: NMR relaxation rates after jet-cooking. The surface sizing barley starch NMR relaxation curve is missing some data points due to measurement set-up problems.

Figure 2: Viscosities measured after jet-cooking.

will be demonstrated later, but some of the increased relaxation rate is probably also related to the structure of the starch. The coating binder starch stands out from the measured starches in that its R_2 value is very high even in $T > 70^{\circ}\text{C}$, whereas the R_2 values of all the other starches at high temperatures ($70\text{--}90^{\circ}\text{C}$) are quite low ($R \approx 1.0\text{--}1.5\text{ s}^{-1}$).

At the beginning of this study, it was expected that jet-cooking would enable the barley starch to become more highly gelatinized than in the case of atmospheric batch cooking, which would be reflected in the amount of retrogradation and thus in the R_2 values. In addition, it was expected that the cooking temperature and speed would be reflected in the NMR measurements. Based on this data, it seems that barley starch retrogrades

quickly with decreasing temperature, despite being “well-cooked”.

The formation of amylose-lipid complexes after jet-cooking is likely an explaining factor for the differences between the otherwise similar wet-end potato and barley starch. In a study by Fanta et al. (2002), potato starch did not form these complexes, whereas wheat starch, which is a cereal starch like barley, did form such complexes. Another probable factor for these differences is that cereal starches are known to contain more amylose than potato starch, which causes them to retrograde faster due to an amylose network forming into the solution (BeMiller and Maurer 2005).

Figure 2 shows the viscosities measured from the starch solutions after jet-cooking. The starches cooked at

Table 2: Linear correlation of R_2 values and viscosities measured after jet-cooking for each jet-cooked sample.

Starch	Cooking conditions	Correlation
Wet-end Barley	140 °C	0.58
	120 °C	0.89
	140 °C, slower cook	0.57
Wet-end Potato	120 °C	0.52
Surface sizing Barley	140 °C	0.99
Coating binder Barley	140 °C	0.98

the lower temperature have the highest viscosities. This was to be expected, because it is known that increasing cooking temperature can cause the starch chains to break down, which reduces viscosity (Lehtinen 2000). The barley starches cooked at 140 °C all have quite a similar viscosity behavior, even though they (wet-end, surface sizing and coating binder) are structurally different from each other. Changing the cooking speed of wet-end barley starch did not have an effect on the viscosity, just as it did not have an effect on the NMR relaxation rates. This probably means that such a small change (1.6 $\rightarrow$ 1.0 kg/min, i. e. 60 %) in jet-cooking speed did not have a meaningful effect on the starch properties.

By comparing Figures 1 and 2, it seems that the NMR curves and viscosity curves do not correlate with each other. This is most pronounced in the case of wet-end potato starch, where the post-cooking R_2 value remained almost constant but the viscosity increased rapidly with decreasing temperature. To gain more information about the correlations between the R_2 values and viscosity, linear correlations were calculated for each sample. The R_2 and viscosity values used for the calculations were picked in such a way that the temperature difference at which they were measured was as small as possible ($\Delta T < 1^\circ\text{C}$). This procedure yielded 4–6 comparable points per sample for the calculations.

As seen from Table 2, the R_2 values and viscosities of the surface sizing and coating binder starch samples correlate highly. However, this correlation is not present in the wet-end starch samples. I. e., sometimes the R_2 values correlate with viscosity and sometimes they do not. The reason for this is unclear.

Based on the inconsistent correlation of R_2 values and viscosities, and based on Figures 1 and 2, it is interpreted that in these starch-water systems, the changes in R_2 values are dominated by changes in the structural properties of the starch, and that the effects of temperature (Arrhenius effect) and viscosity on relaxation rates are not visible.

Such an interpretation of the relationship of viscosity and NMR relaxation comes into some conflict with other studies about similar topics, such as the study by Nivellet et al. (2019), where viscosity and temperature play a significant role in explaining the NMR relaxation results. One explanation for this difference could be that in our studies the solids content is much lower than in the case of bread-making studies, which has an influence not only on the viscosity but also on the molecular dynamics between water and starch.

NMR relaxation and viscosity during storage

The R_2 and viscosity results for the wet-end potato and barley starches stored at 40, 60 and 90 °C are shown in Figures 3–8. The relaxation rate of potato starch (Figure 3) stored at all temperatures remained at a very low R_2 value throughout the whole period, which likely means that there was no retrogradation occurring. The viscosity of the potato starch samples held at 40 and 60 °C stayed almost constant, indicating that no changes happened. However, at 90 °C, the viscosity decreased over time, which probably means that the starch chains degraded over time due to the high temperature.

For the wet-end barley starch (Figure 4), the relaxation rates remained rather constant over time, as they did for the potato starch jet-cooked at the same temperature. The only difference is that now the “starting points of R_2 ” are different because of how the barley starch retrogrades after cooking. In the case of the sample stored at 60 °C, after 21 h of storage, the R_2 value “peaked”, which might be a measurement error. Due to the small number of consecutive measurements ($n = 5$), one measurement point is not enough to draw any conclusions. The viscosities remained quite constant. The results indicate that neither retrogradation nor chain degradation happened on a meaningful level at any storage temperature.

For the wet-end barley starch cooked at a higher temperature (Figure 5), the viscosity was much lower, as was described before (Figure 2), and the R_2 and viscosity values remained quite constant over time, as was the case for the same starch cooked at a lower temperature.

Changing the cooking speed of the wet-end barley starch (Figure 6) did not have a significant effect on the viscosity or R_2 values.

The surface sizing barley starch samples (Figure 7) might have undergone some retrogradation at 40 and 60 °C because their R_2 values increased over time, but the changes were small. Viscosities remained very low throughout the storage for all temperatures.

Figure 3: NMR relaxation rates and viscosities for wet-end potato starch jet-cooked at 120°C and stored at different temperatures.

Figure 4: NMR relaxation rates and viscosities for wet-end barley starch jet-cooked at 120°C and stored at different temperatures.

Figure 5: NMR relaxation rates and viscosities for wet-end barley starch jet-cooked at 140°C and stored at different temperatures. Some data points from viscosity at 90°C are missing due to measurement set-up issues.

After one day in storage, a sediment began to form in the surface sizing barley starch sample at 90°C . This was interpreted as high-temperature retrogradation

(HTR), which is known to happen for some starches during storage (Davies et al. 1980, Fanta et al. 2002). Cereal starches, such as barley, have more lipids than potato

Figure 6: NMR relaxation rates and viscosities for wet-end barley starch jet-cooked more slowly at 140°C and stored at different temperatures.

Figure 7: NMR relaxation rates and viscosities for surface sizing barley starch jet-cooked at 140°C and stored at different temperatures.

starch, and lipids are known to have an important role in the HTR mechanism (Fanta et al. 2002). The forming sediment is probably comprised of amylose-lipid complexes, which have been described in previous studies (Davies et al. 1980, Fanta et al. 2002, Nivellet et al. 2019, Putseys et al. 2009), and are known to form at 90°C . The sediment formation was not visible in these R_2 or viscosity results. This was perhaps due to the samples being mixed before measuring, which resuspended the sediment.

The coating binder barley starch (Figure 8) expressed much of the same behavior as the surface sizing barley starch (Figure 7): a sediment formed at 90°C after one day of storage, viscosities remained stable in all temperatures, and the samples at 40 and 60°C remained stable based on the R_2 values. However, the sample at 90°C exhibited a clear decrease in R_2 value over time, which might be a result of the HTR sediment formation. Why this happened for the coating binder starch, but not for the surface sizing

starch, is unknown. It is important to note that the scale of the R_2 y-axis in Figure 8 is different from Figures 3–7.

To summarize, the relaxation rates and viscosities for most samples did not significantly change over time when stored at a constant temperature. The R_2 and viscosity results for wet-end starch samples stored at 40, 60 and 90°C (Figures 3–6) were quite similar for all of the samples. This was interpreted to mean that the wet-end starches generally remained stable at all temperatures and that significant retrogradation did not occur. The exception to this behavior were the surface sizing and coating binder barley starches stored at 90°C , which exhibited formation of a sediment starting after 1 day of storage.

High-temperature retrogradation samples

Figure 9 shows the R_2 values for the supernatant and sediment separated from the surface sizing and coating binder

Figure 8: NMR relaxation rates and viscosities for coating binder barley starch jet-cooked at 140 °C and stored at different temperatures.

Figure 9: NMR relaxation rates for the supernatant and sediment separated from the surface sizing and coating binder barley starches jet-cooked at 140 °C after 2 days of storage at 90 °C.

barley starch HTR samples. The solids content of the sediment and supernatant samples are shown in Table 3 along with the solids content before separating the phases. As could be expected, the consistency of the supernatant was lower than the consistency of the original solution after cooking, and the consistency of the sediment was higher.

It can be seen from Figure 9 that the sediments of both starches have a much higher R_2 value than the supernatants. As will be shown in the next subsection, consistency does have an effect on the R_2 value but such a large difference as seen in Figure 9 can only be explained by a difference in the structure of the supernatant and sediment. I.e., the sediment had a large amount of retrograded solid material, and the supernatant had mostly soluble material. The supernatant probably contained un-retrograded, solubilized amylopectin, which is known to retrograde slowly (Wang et al. 2015), and the sediment contained retrograded amylose or amylose-lipid complexes, as has been reported previously for corn, rice and wheat starches (Fanta et al. 2002).

Table 3: Solids content of the supernatant and sediment separated from the surface sizing and coating binder barley starch HTR samples.

Starch	Solids content (wt-%)		
	Before separation	Supernatant	Sediment
Surface sizing	12.4	11.6	14.0
Coating binder	20.9	19.8	25.9

The reason why only surface sizing and coating binder barley starches formed a significant amount of HTR sediment at 90 °C storage, but the wet-end barley starches did not, although they should have approximately the same lipids content, could be that the lower molecular weight of the surface sizing and coating binder starches facilitates HTR. Shorter chains are known to predispose a starch to retrogradation via amylose-lipid complex formation (Putseys et al. 2009).

Effect of solids content on NMR relaxation

The starch solution's solids content and the NMR relaxation rate have a linear relationship, as is evident from Figure 10. As the solids content decreases, the proportional amount of water interacting with the starch also decreases. This leads to increased overall proton mobility and thus decreased R_2 values.

Conclusions

The NMR-relaxometric method used in this study was sensitive to differences between jet-cooked starches based on their botanical origin (potato vs. barley), their modifica-

Figure 10: Relationship between the NMR relaxation rate and solids content measured from surface sizing barley starch at 27 °C.

tion (high molecular weight and cationic vs. low molecular weight and oxidized) and solids content. However, the method was not able to detect differences between different cooking temperatures, and the method was not sensitive to viscosity changes.

Increased jet-cooking temperature reduced the wet-end barley starch's viscosity considerably, especially when the starch cooled below 60 °C. Changing the cooking speed from 1.6 kg/min to 1.0 kg/min had no effect on the wet-end barley starch's post-cooking NMR relaxation or viscosity, which probably means that such a small cooking speed difference is irrelevant for the starch's properties.

Based on this data, when just gelatinization and retrogradation are concerned, there is no difference between jet-cooking at $T \geq 120$ °C and batch cooking at 95 °C, because no differences were visible in the NMR relaxation rates. However, jet-cooking at different temperatures was effective for changing the viscosity of the starch solution, which is an important factor for starch in papermaking.

Barley starches showed signs of rapid retrogradation even after jet-cooking at a high temperature, whereas potato starch did not show such an effect. These differences can probably be explained by two factors. First, barley starch contains more amylose than potato starch, which enables it to form a more extensive amylose network after cooking. Second, barley starch contains more lipids than potato starch, which facilitates the formation of amylose-lipid complexes in barley starch that are absent in potato starch.

The storage temperature of 60 °C proved to be the best for all of the starches if the goal is a stable solution after cooking, i. e., the NMR relaxation and viscosity remain as constant as possible. At 90 °C storage, HTR or possible chain degradation can occur, which is undesirable. Storage at 40 °C did not seem to cause any problematic phenomena during these experiments, but the retrogradation of barley starch does advance further as the temperature

goes down, so a lower temperature, such as 40 °C, should still be avoided.

The HTR sediment formed in surface sizing and coating binder barley starches is probably comprised of amylose-lipid complexes. The NMR relaxation data from the HTR supernatant and sediment supports the conclusion that the supernatant contains solubilized starch, whereas the sediment contains more highly-ordered, crystalline or amorphous, solid starch.

In future studies, it would be interesting to determine the ratio of amylose, amylopectin and lipids in the HTR sediment and supernatant in order to gain a more thorough understanding of the HTR mechanism. In addition, using additional measurement tools, such as DSC, to verify the NMR-relaxometry results regarding the degree of starch retrogradation would be useful.

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