

# Determining the heat of reaction of kraft pulping

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**ABSTRACT:** Kraft pulping is accompanied by a gradual but significant exothermic heat of reaction. Most of the exothermic heat results from the neutralization of carboxylic acids formed by the degradation of carbohydrates. The exothermic heat was measured in a laboratory digester for both softwood and hardwood cooks. The measured values of the heats of reaction at a final H factor of 1200 were  $-93 \pm 31$  kcal per kilogram of wood dissolved for softwood and  $-148 \pm 28$  kcal per kilogram of wood dissolved for hardwood. These results were used in a spreadsheet model to estimate the energy balance and the maximum temperature rise to be expected in batch kraft digesters.

**Application:** Knowing the magnitude and generation rate of the exothermic heat is important for the proper control of digesters.

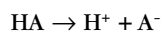
Heat is evolved during kraft pulping, as generally known, but the extent of this heat release has not been adequately defined. A better understanding of this effect is needed for engineers to develop improved digester control programs and properly size relief systems. If a significant amount of heat is released near the end of the cook, changes may be required in the current design of the digester relief system. If most of the heat is released at the beginning of the cook, during the heat-up phase, the exothermic heat would have minimal impact on digester overpressurization.

Scott describes an automatic control system for batch digesters that includes a pressure relief because "once the delignification temperature has been reached, the system becomes exothermic, requiring relief to maintain the temperature" [1]. Sherman and Prough describe a control system for a continuous digester that measures the temperature rise in the cooking zone resulting from the exothermic reactions and that uses this measurement to determine the degree of delignification [2].

Exothermic reactions in kraft pulping result mostly from the neutralization of native wood acids by alkali and the neutralization of acids that form during the cook from the degradation of carbohydrates and lignin. The primary carbohydrate degradation products have been identified as hydroxycarboxylic acids, such as glucoisaccharinic acid [3]. The total amount of acids produced varies with species and has been found to be 30% higher in birch than in pine [4]. Most of the alkali charged for a cook is used to

neutralize these acids. Sjöström states that 60–70% of the charged alkali is used in neutralizing hydroxycarboxylic acids, about 10% is used to neutralize uronic and acetic acids, and 20–30% is consumed by the degradation products of lignin [5]. All of these reactions can be expected to produce a certain amount of exothermic heat.

The heat generated from the neutralization of a weak acid, such as those formed during pulping, is a result of two chemical reactions [6]. These are as follows:



where  $\Delta H_i$  is the heat of ionization or dissociation of the acid, and



where  $\Delta H = -13.52$  kcal/mole at 25°C. This is the heat of neutralization.

A negative  $\Delta H$  indicates an exothermic reaction. For neutralizing a weak acid, the heat of reaction is equal to:  $\Delta H_i + (-13.52$  kcal/mole). For a representative carboxylic acid such as acetic acid ( $\text{CH}_3\text{COOH}$ ),  $\Delta H_i$  is equal to  $-0.092$  kcal/mole at 25°C, so the heat of neutralization at 25°C is:  $(-0.092) + (-13.52)$ , or  $-13.60$  kcal/mole. **Appendix A** presents a calculation of the exothermic heat based on this information for a kraft process.

While some data exist for the amount of heat released by exothermic reactions in kraft pulping, there does not appear to be any direct determination of this heat reported in the literature. In the work reported here, the amount of heat evolved was measured as the difference in the electrical energy required to heat a

laboratory digester during kraft pulping and the electrical energy required to heat an equivalent thermal mass of water. This procedure is similar to that used for measuring heats of reaction in a calorimeter [7].

## EXPERIMENTAL

### Furnish

Two mill chip supplies were used, a softwood sample from the coastal southeastern United States and a mixed hardwood sample from the Piedmont region of the southeastern United States. After pulping, the composition of the hardwood sample was found to be 37% yellow poplar, 42% oak, 7% maple, 5% basswood, 5% cucumber magnolia, 3% beech, and 1% gum.

The chips were screened on a Williams chip screen, and the oversized ( $>1$  in.) and undersized fines ( $<0.25$  in.) fractions were discarded. We characterized the chips with respect to moisture content by drying triplicate samples in an oven at 105°C.

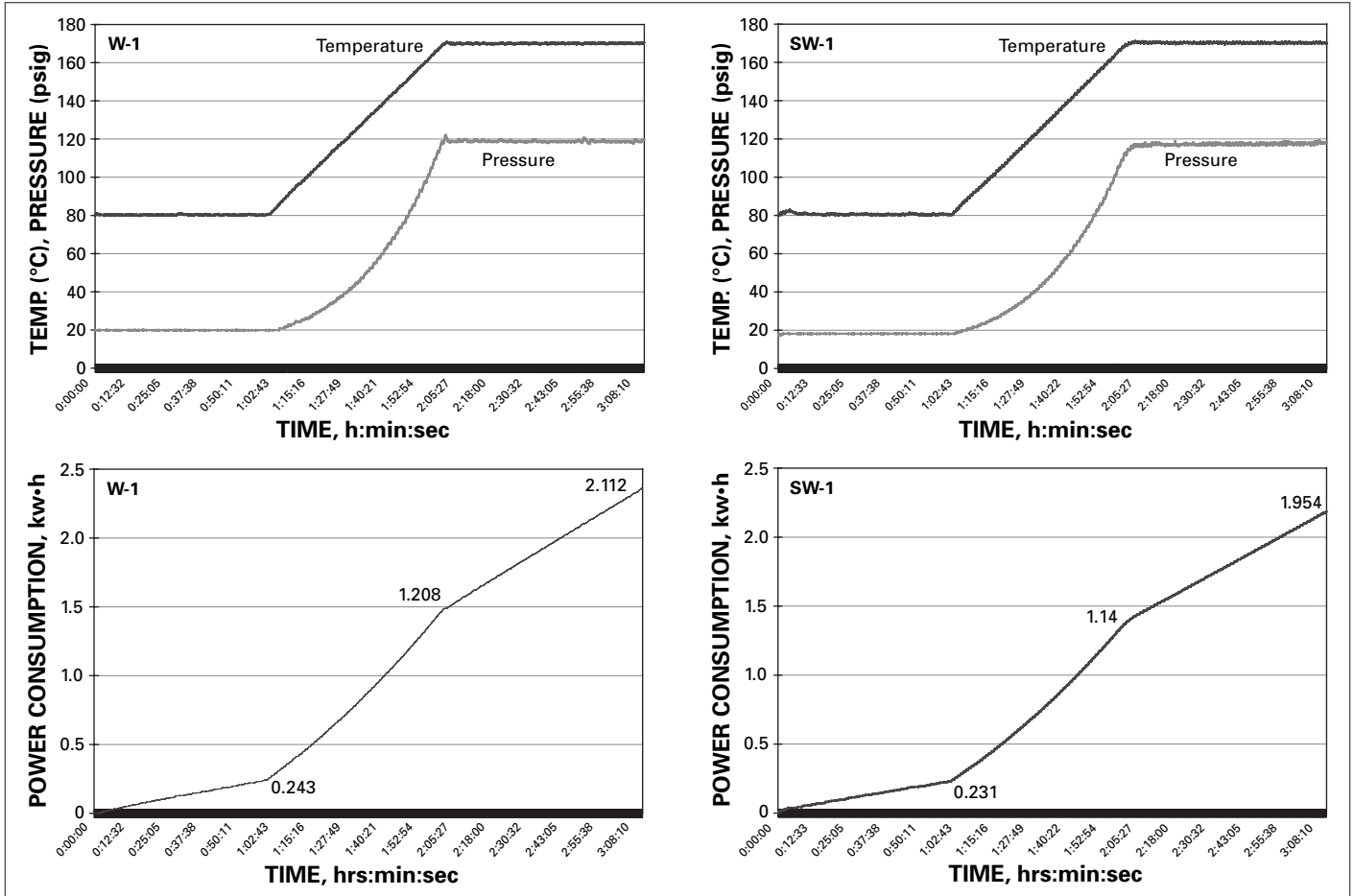
### Lab digester

A 6 L circulating digester with indirect electric heating was used for these experiments. Pressure, temperature, and H-factor were continuously monitored and recorded; data points were collected every 5 s. A power recording transducer measured the power input to the heater. The total energy consumption was calculated by numerical integration of the power signal with respect to time.

### Cooking

Two solutions, one of NaOH and one of  $\text{Na}_2\text{S}$ , were made in the lab from reagent-grade chemicals dissolved in deionized water. The solutions were titrated with an

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1. Temperature and pressure (upper) and power consumption (lower) for the W-1 and SW-1 cooks (left and right, respectively).

	Active alkali, %	Sulfidity, % of AA	Screened Kappa no.	yield, %	Rejects, %	Total yield, %
Water						
W1-W6	—	—	—	—	—	—
Softwood						
SW-1	21.1	37	33.6	44.6	0.01	44.6
SW-2	21.1	37	34.2	44.9	0.01	44.9
SW-3	21.1	37	35.5	44.9	0.01	44.9
SW-4	21.1	37	35.5	44.1	0.004	44.1
Hardwood						
HW-1	16.8	30	14.7	45.6	0.01	45.6
HW-2	16.8	30	14.5	46.0	0.01	46.0
HW-3	16.8	30	14.8	46.1	0.01	46.1

\*Percentages are % on o.d. wood for AA, screened yield, rejects, and total yield.

## I. Cooking conditions, yields, and kappa numbers for the cooks (at 170°C).

automatic titrator according to the standard “ABC” test. The required amount of each solution was measured out for each cook, and the mixture was diluted with deionized water to reach a total liquor:wood ratio of 4:1. The charge of chips to the digester was 1000 o.d. grams.

For all cooks, the water or chips and liquor were added to the digester, heated to 80°C, and held at this temperature for 1 h to ensure that the entire mass was always at a constant start-

	Amt., kg	Cp, kcal/ K mole	TEMP., °C			ENERGY,	
			T <sub>initial</sub>	T <sub>final</sub>	DT	kcal	kW·h
Chips	1.00	0.33	80	170	90	29.7	—
Liquor	4.00	0.98	80	170	90	353	—
Digester	17.9	0.12	80	170	90	193	—
<b>Sum</b>						<b>576</b>	<b>0.67</b>

## II. Estimate of the energy required to heat the M/K lab digester from 80°C to 170°C.

ing temperature. The cooking schedule consisted of heating from 80°C to 170°C in 60 min and holding the temperature at 170°C for 70 min. This schedule applied to both softwood and hardwood. The digester was vented briefly when it reached 100°C to relieve noncondensable gases.

For the reference water “cooks,” a mass of water thermally equivalent to the total mass of the liquor at the 4:1 ratio was measured out. We conducted tests in the digester by heating equal masses of the liquor and water and measuring the energy to determine if the specific heats of these two differed. These tests showed that there was no difference in specific heat between the liquor and water within the accuracy that could be determined with the experimental apparatus. An additional amount of water, thermally equivalent to the mass of the chips (assuming a specific heat of 0.33 kcal/kg °C), was also added to give a total mass of water thermally equivalent to the mass of the liquor and chips. This value of specific heat for wood was

established by Dunlap, as reported by Hawley and Wise [8].

## Pulp processing

After each cook, the chips were disintegrated and screened on a 0.20 mm slotted flat screen. The screen rejects were collected, dried, and weighed. The accepted pulp was collected, thickened, and weighed. Its consistency was measured to determine a screened yield based on the dry weight of the chips. The percentage of screen rejects based on the total pulp weight was also calculated. The total yield was calculated as the screened yield plus the screen rejects. The kappa number of the pulp was determined according to TAPPI T 236.

## RESULTS

The cooking conditions, yields, and kappa numbers for the kraft cooks are shown in **Table I**. For each cook, the temperature, pressure, and cumulative energy consumption were recorded every five seconds. Representative graphs of the data for a water reference cook (W-1) and a softwood kraft cook (SW-1) are shown in **Fig. 1**. The graphs reflect the hold at a constant temperature of 80°C for 1 h, then the programmed heat from 80°C to 170°C in 1 h, and the hold at 170°C for 70 min. The energy profiles show the accumulation of energy as kW·h for heating up and maintaining the temperature as a function of time.

In a small lab digester with a high surface-to-volume ratio, the heat losses are high, as evidenced by the continual rise in energy from 2 h on, when the cooking temperature had been reached. This energy is required to maintain the temperature as a result of heat losses in the system. The energy requirement that would be estimated to heat the digester shell, liquor, and chips from 80°C to 170°C is calculated in **Table II** as 0.67 kW·h. The actual measured values were 1.1–1.2 kW·h. The difference is an indication of the degree of heat loss.

The numbers shown on the energy charts represent the cumulative energy inputs for each part of the cycle. In the two lower graphs of the figure, the first value shown, at 1 h, is the energy required to achieve and maintain the constant temperature of 80°C for the initial holding period. The value shown at 2 h is the energy accumulated up to that

Kraft cook	Energy, kW·h	Water cook	Energy, kW·h
SW-1	1.140	W-1	1.208
SW-2	1.140	W-2	1.185
SW-3	1.146	W-3	1.179
SW-4	1.148	W-4	1.185
HW-1	1.132	W-5	1.208
HW-2	1.117	W-6	1.202
HW-3	1.110	—	—

III. Energy consumption for 60 min heat-up time.

point minus the value from the initial holding period. This value represents the energy to heat up from 80°C to 170°C in 1 h. The final value, at 3 h, 10 min, is the total energy at that time minus the energy for the initial holding period. This value represents the total energy consumption for the 130 min cook cycle.

The energy figures for the softwood kraft cooks, hardwood kraft cooks, and water reference cooks are shown in **Table III** for the 60 min heat-up time and in **Table IV** for total 130 min cook. The mean values and variances were calculated for each group. The mean value of each set of kraft cooks was compared separately to the mean value from the water cooks by a two-tail *t* test to determine if they were significantly different. In each case, the energy consumption in the kraft cooks was significantly different from the energy consumption for the water cooks at a confidence interval of 95%. The lower energy consumption for the kraft cooks compared to the water cooks indicates that exothermic reactions that take place during the kraft cooks supply some of the heat for the reaction. The difference is a measure of this exothermic heat.

The exothermic heats of reaction with a 95% confidence interval are shown in **Table V** for both the initial 60 min heat-up to temperature and for the total cook. The total heat of reaction based on the amount of wood dissolved is also shown, determined from the average yield loss for each of the respective cooks.

## DISCUSSION

The calculated values for the total heat of reaction,  $-93 \pm 31$  kcal/kg of wood dissolved for softwood and  $-148 \pm 28$  kcal/kg of wood dissolved for hardwood, compare favorably with a theoretical

Kraft cook	Energy, kW·h	Water cook	Energy, kW·h
SW-1	1.954	W-1	2.112
SW-2	1.969	W-2	2.047
SW-3	1.986	W-3	2.017
SW-4	1.964	W-4	2.024
HW-1	1.934	W-5	2.021
HW-2	1.932	W-6	2.032
HW-3	1.939	—	—

IV. Energy consumption for 130 min total cook time.

Kraft cook	Yield, %	During heat-up, kcal/kg <sup>a</sup>	For total cook, kcal/kg <sup>a</sup>	For total cook, kcal/kg <sup>b</sup>
SW	44.6	$-42 \pm 13$	$-52 \pm 17$	$-93 \pm 31$
HW	46.0	$-62 \pm 19$	$-80 \pm 15$	$-148 \pm 28$

<sup>a</sup>kcal/kg of wood charged. <sup>b</sup>kcal/kg of wood dissolved.  
BTU/lb of wood = 1.8 × kcal/kg of wood.

V. Calculated heats of reaction with 95% confidence interval.

value of  $-113$  kcal/kg of wood dissolved for neutralization of carboxylic acids (Appendix A). About 80% of the total was evolved during the heat-up time. The heat of reaction evolved gradually throughout the course of the cook, with a faster rate during the time to temperature and a slower rate at cooking temperature. The heat of reaction for the hardwood was 60% more than that for the softwood. Hardwoods typically have a higher hemicellulose content than softwoods, which would likely result in more acid formation from carbohydrate degradation.

## Energy balance model

The heat of reaction determined can be used to predict batch digester conditions and determine control conditions. One model incorporating these results was developed to determine the total energy balance. The initial energy state of the digester and contents was determined by a calorimetric mixing cup calculation using the initial temperatures of the chips (24°C) and liquor (88°C) as they are added to the digester.

$$\sum C_{p_i} M_i (T_i - T) = 0 \quad (1)$$

where

- $M_i$  = mass of material *i*
- $C_{p_i}$  = heat capacity of material *i*
- $T_i$  = initial temperature of material *i*
- $T$  = mixing cup temperature of system.

Specific heat data for the wood,

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liquor, and digester components were used to determine the amount of energy required to increase the digester temperature. Since the heat released from the pulping exothermic reaction is primarily the result of the neutralization of carboxylic acids, the rate can be approximated by the alkali consumption [3, 4]. The alkali profile as a function of time was obtained from several sources [9-13]. The alkali consumption can be represented by three phases, similar to the three main phases of delignification: initial, bulk, and residual. The initial phase, terminated at an H-factor of 100, corresponds to about 70% of the alkali consumption, during which phase about 15% of the lignin is reacted. During the bulk phase from about 100 to 1000 H-factor, 70% of the lignin reacts, and the remainder of the pulping exotherm is expended. In the residual phase, another 15% of the lignin may be reacted.

The lignin content or alkali consumption can be represented as a function of H-factor with an equation of the form:

$$Y = m \cdot 10^{cx} \quad (2)$$

where  $Y$  is either the lignin content or the alkali consumption and  $m$  and  $c$  are constants specific to various phases of the cook being modeled.

The heat of reaction (assumed to be proportional to the alkali consumption) can be predicted at a specific H-factor by Eq. 3 for the initial phase (up to 100 H-factor) and by Eq. 4 for the bulk phase, which is the rest of the cook.

$$Y = 144 \cdot 10^{-0.00523 \cdot \text{H-factor}} \quad (3)$$

$$Y = 60.84 \cdot 10^{-0.00149 \cdot \text{H-factor}} \quad (4)$$

where  $Y$  is the heat of reaction for either the initial or bulk phase.

Energy balances at any point in the cook can be calculated from heat inputs from direct steam and the exothermic pulping reaction and heat losses from venting and radiant and conductive cooling. These calculations are based on the assumption that there is sufficient headspace in the digester for compressible gas volumes. A hydraulically full digester is a different case: in this situation, a small temperature increase will lead to a dramatic pressure increase. OSHA has recently issued revised guidelines for digester control to prevent mills from

completely filling a digester [14].

The model was used to predict a worst-case condition under the assumption that operation was adiabatic for a typical hardwood digester. The digester weighed 100 tons (90,720 kg) with 10,000 lb (4540 kg) of insulation. The wood charge was 35 o.d. tons at 43% moisture. The charge of white liquor was 52 m<sup>3</sup> (13,463 gal) and 15 m<sup>3</sup> (4000 gal) of black liquor at an initial temperature of 88°C (190°F). Extending the cook to 9.5 h shows that a total temperature increase of 12.2°C (54°F), corresponding to 32 psig (221 kPa), would be experienced as a result of the pulping exotherm.

Another application of the model was used to predict the worst-case scenario for another mill digester that was pulping 93% softwood and 7% hardwood. The cooking conditions were 21 o.d. tons of chips, 7265 gal of white liquor (100 g Na<sub>2</sub>O/L), and 6472 gal of black liquor. The mass of the digester was 60 tons with 30 tons of insulation. The heat loss was assumed to be 7000 BTU/min (7380 KJ/min). About 16-17 thousand tons/h (588-625 lb/min) of steam was available to bring the digester to the cooking temperature of 172°C in 90 min. The model was used to predict the temperature and pressure after 9.5 h, representing the case of a bottled-up digester. For this case, a maximum temperature of 173.6°C and a pressure of 869 kPa (126 psig) were reached at the end of the extended time.

## Mill results

Several tests were also conducted in actual mill batch digesters to verify the extent of the exothermic heat of reaction. A well-insulated digester was "bottled-up" at three different points during a cooking cycle, and the temperature and pressures were monitored for an extended time, up to 11 h. When the digester was bottled at 20 H-factor or 149°C, the maximum temperature reached was 171°C and a pressure of 100 psig (689 kPa).

Bottling the digester at 750 H-factor, or 163°C, resulted in a final temperature of 177°C and a pressure of 150 psig. When the digester was bottled at 1250 H-factor, or 174°C, the final temperature did not exceed 177°C, and the final pressure was 120 psig. These results agree well with the predicted model results

based on the heat of reaction determined by this study.

## CONCLUSIONS

There is a significant, measurable exothermic heat of reaction during kraft pulping. This heat results primarily from the neutralization of carboxylic acids already present in the wood or formed during the cook. The heat of reaction was determined in lab tests to be -93±31 kcal/kg of wood dissolved for softwood and -148±28 kcal/kg of wood for hardwood.

Most (80%) of the exothermic heat is given off during the heat-up phase, and there is minimal effect in the latter stages of a cook. The exothermic heat of reaction is evolved gradually and does not result in pressure spikes as long as the digester is not hydraulically filled.

These results can be used to model the heat balance for batch digesters. This model can be used in turn to design appropriate control systems. **TJ**

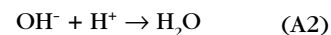
## APPENDIX A: HEAT OF REACTION

To calculate of the heat of reaction for neutralizing hydroxycarboxylic acids, use acetic acid (CH<sub>3</sub>COOH) as a representative carboxylic acid.

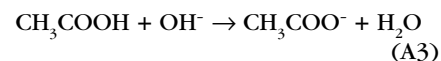
The dissociation reaction for acetic acid, A1, and the neutralization reaction for acid and base, A2, with the heats of reaction ( $\Delta H$ ) at 25°C are added together to give the overall neutralization reaction, A3 (data from Farrington and Alberty [6], p. 228):



where  $\Delta H_{25} = -0.092$  kcal/mole.



where  $\Delta H_{25} = -13.51$  kcal/mole.

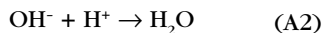


where  $\Delta H_{25} = -13.60$  kcal/mole.

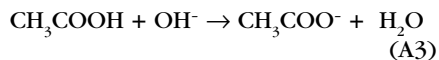
The heat of reaction at 170°C is calculated from  $\Delta H_{170} = \Delta H_{25} + \Delta C_p(25 - 170)$ :



where  $\Delta C_p = -0.037$  kcal/K mole. At 170°C, or 443.15°K,  $\Delta H_{170} = 5.27$  kcal/mole.



where  $\Delta C_p = 0.047$  kcal/K mole. At  $170^\circ\text{C}$ ,  $\Delta H_{170} = -20.32$  kcal/mole.



where  $\Delta H_{170} = -15.0$  kcal/mole.

This result can be applied to softwood kraft pulping where AA= 21.0, percent sulfidity = 37%, effective alkali (EA) = 17.1%, and yield = 45.0%. EA on wood =  $1 \text{ kg} \cdot 0.171 = 0.171 \text{ kg}$  as  $\text{Na}_2\text{O}$ , or  $0.221 \text{ kg}$  as NaOH, or 5.52 g-moles NaOH.

From Sjöström [5], 75% of the effective alkali goes to neutralize acids formed during pulping. Therefore, we have  $5.52 \text{ g-moles} \cdot 0.75 = 4.14 \text{ g-moles}$ .

The heat of reaction for neutralization is:  $(4.14 \text{ g-moles/kg wood}) \cdot (-15.0 \text{ kcal/mole}) = -62.1 \text{ kcal/kg wood}$ . At 45.0% yield, this is  $-113 \text{ kcal/kg}$  of wood dissolved, or  $-203 \text{ BTU/lb}$  of wood dissolved.

## ACKNOWLEDGEMENT

This work was originally supported by the Batch Digester Task Force of the American Forest & Paper Association.

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Received: August 1, 2005  
Accepted: October 8, 2005

This paper is also published on TAPPI's web site <[www.tappi.org](http://www.tappi.org)> and summarized in the December *Solutions! for People, Processes and Paper* magazine (Vol. 88 No. 12).

## INSIGHTS FROM THE AUTHORS

When a batch digester incident occurred at a mill, it raised the question of whether or not the control systems commonly used are adequate to contain the reactions that take place during kraft pulping. One issue was the amount of reaction heat that could be generated during kraft pulping. Although there was some process design information on the heat of reaction, this information was not well known and was not adequately documented, particularly not to the satisfaction of regulatory authorities. Consequently, we decided to develop some experiments, measure this quantity directly, and document the information.

The biggest challenge was finding a way to measure the heat of reaction directly under realistic kraft pulping conditions. We decided to use a laboratory digester as a type of calorimeter. We would measure the electrical energy required to heat the system during kraft pulping and compare this amount to the energy required to heat an equivalent amount of water in which no chemical reactions were taking place. The difference would be a measure of the exothermic heat generated during kraft pulping.

We found that the amount of exothermic heat generated is fairly significant, which was not so well known. This heat has not always been taken into account in determining digester heat balances. This exothermic heat is expended mostly in the initial part of the cook and does not present any problems for a runaway type of reaction.

Now that there are some quantitative values regarding the heat of reaction, mills can use these numbers in calculating digester heat balances and designing control systems. No additional work is planned. This study has already been used by regulatory authorities to revise the standards that govern the control of batch digesters.

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