

**DEACETYLATION OF *Eucalyptus globulus* ACETOSOLV PULPS IN AQUEOUS MEDIA: A KINETIC STUDY**Carlos VILA<sup>1</sup>, Sonia DAPÍA<sup>2</sup>, Valentín SANTOS<sup>3</sup> and Juan Carlos PARAJÓ<sup>4,\*</sup>

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Received June 1, 2001  
Accepted July 31, 2001

Pulps obtained from *Eucalyptus globulus* wood in HCl-acetic acid-water (Acetosolv processing) were subjected to aqueous processing at a liquor-to-solid ratio of 8 kg/kg and 160–190 °C, in order to explore the suitability of this kind of treatment for pulp purification. Both deacetylation and hemicellulose removal were caused by the treatment, whereas cellulose was not significantly affected. The concentration profiles of reaction products (glucose, xylose and acetic acid) were determined, and the experimental data were modelled using pseudohomogeneous, first-order kinetics. The dependence of kinetic coefficients on temperature was established by means of Arrhenius-type equations.

**Keywords:** Acetic acid pulping; Acetosolv delignification; *Eucalyptus globulus* wood; Deacetylation; Hemicellulose removal; Cellulose; Kinetics.

Pulping technologies based on the utilisation of organic solvents (organosolv pulping) allow the fractionation of the lignocellulosic raw materials, leading to a solid phase enriched in cellulose and to liquors containing hemicellulose- and lignin-degradation products. Both phases can be used for making commercially valuable final products<sup>1</sup>.

Acetosolv pulping is an environmentally friendly pulping technology based on the utilisation of media made up of acetic acid (up to 95%) in the presence of 0.1–0.5% hydrochloric acid (which acts as a catalyst). This process allows selective production of pulps with low contents of hemicellulose and lignin, favourable physicochemical properties, and good pulp yields<sup>2–4</sup>.

A comparatively high content of acetyl groups Acetosolv pulps is one of their main drawbacks. For example, in the manufacture of dissolving pulps by a typical “totally chlorine free” (TCF) bleaching sequence, the acetyl groups would be hydrolysed at the alkaline stage, leading to NaOH consumption. A possible alternative is to reduce the acetyl group content of

Acetosolv-delignified pulps by aqueous treatment, which could be compatible with the washing stages prior to alkaline bleaching stages. As an additional advantage, this operational strategy promotes simultaneous removal of xylan (the most important component of hemicelluloses in hardwoods), leading to pulps with improved purity. This is of primary importance in the manufacture of cellulose derivatives, because here the hemicellulose content of pulps must be reduced below a given threshold in order to limit the solution haze caused by degradation of xylose and furfural<sup>5</sup>. The aqueous treatment can be carried out alternatively or additionally to other stages for hemicellulose reduction based on utilisation of enzymes<sup>6-8</sup> or cold caustic extraction.

In aqueous treatment of acetyl-containing substrates (hydrothermolysis), the degradation of both acetyl groups and hemicelluloses is caused by catalytic action of hydronium ions. In the first reaction stages, the hydronium ions are generated from water, whereas acetic acid from acetyl groups is the most important source of catalytic species in further reaction stages<sup>9</sup>. The fundamentals of acetyl group and hemicellulose removal from pulps obtained in organic acid media are closely related to autohydrolysis of wood, the first treatment stage in the prehydrolysis-kraft process (a technology leading to high-quality pulps with improved susceptibility to bleaching)<sup>10</sup>.

In the reaction media, polysaccharides in the substrates (hemicelluloses and cellulose) may react to give monosaccharides, and the sugars can be decomposed under harsh conditions<sup>11</sup>.

This work deals with the experimental assessment and kinetic modelling of the hydrolytic effects caused by water treatment on several fractions of Acetosolv pulps (cellulose, hemicelluloses and acetyl groups). The time course of the corresponding reaction products (glucose, xylose and acetic acid) in isothermal treatment (at 160–190 °C) was established, and the experimental data were correlated with operational variables (reaction time and temperature) using pseudohomogeneous, first-order kinetics.

## MATERIALS AND METHODS

### Raw Material

*Eucalyptus globulus* wood chips were provided by ENCE (Pontevedra, Spain). Wood chips were screened to separate a particle fraction below 2 mm, homogenised in a single lot to avoid compositional differences and stored.

## Pulping

The experimental conditions chosen for Acetosolv pulping of *Eucalyptus* wood were selected on the basis of the results of Abad *et al.*<sup>12</sup> (Table I). Pulps were successively washed with warm 95% acetic acid and water, treated in a UltraTurrax T-50 defibrator (IKA Labortechnik, Germany) at 5 000 rpm for 30 s, screened in a Somerville device (with 0.8 mm square holes) and air-dried before analysis.

## Analysis and Physicochemical Characterization of Pulps

The composition and physicochemical properties of pulps were determined using the following analytical methods: moisture, ISO 638:1978; cellulose (as glucan), xylan and acetyl groups, by HPLC analysis of glucose, xylose and acetic acid, respectively, contained in the products of quantitative acid hydrolysis carried out according to the TAPPI T13m assay (see below); furfural, by direct HPLC analysis of liquors (see below); residual lignin expressed in terms of *kappa* number, ISO 302:1981; and acid-soluble lignin, method of Maekawa<sup>13</sup>.

## Deacetylation Experiments

Acetosolv-delignified *Eucalyptus* wood and water were mixed at the desired proportions in a Parr reactor with a working volume of 600 ml and heated to the given temperature (in the range of 160–190 °C). The vessel was heated in an external fabric mantle and cooled with an internal stainless steel loop. Temperature was monitored using a thermocouple, and controlled by a PID module. The reaction medium was heated to a desired temperature (heating-up time of 15 min). Zero time was set when the reaction medium achieved the pre-set temperature. At this moment, a sample was withdrawn in order to measure the concentrations of reaction products resulting from conversion of the substrate during the non-isothermal part of the reaction. The data used for kinetic modelling correspond only to the isothermal reaction stage. All the experiments were carried out at a liquor-to-solid ratio (LSR) of 8 g water/g oven-dry solid. The operational variables involved in this study were reaction time ( $\tau$ , min) and temperature of the isothermal reaction stage ( $t$ , °C).

TABLE I  
Experimental conditions selected for wood pulping

Experimental conditions	
Acetic acid concentration, %	95
HCl concentration, %	0.30
Reaction time, min.	90
Liquor to solid ratio, g/g	7
Temperature, °C	110

### Analysis of Deacetylated Pulps

The pulps coming from water treatments were characterised by the same methods listed above for analysis of Acetosolv pulps.

### Analysis of Liquors from Deacetylation Treatments

For direct determination of glucose, xylose, acetic acid and furfural, samples of liquors were filtered through 0.45  $\mu\text{m}$  cellulose membranes and analysed by HPLC with RI and DAD detection using an Aminex HPX 87H column and elution with  $1.8 \cdot 10^{-4}$  M  $\text{H}_2\text{SO}_4$  at 45 °C.

### Fitting of Data

The experimental data were fitted to the equations derived from the proposed mechanism by minimising the sum of the squares of deviations between experimental and calculated data with commercial software using the Newton method.

## RESULTS AND DISCUSSION

### *Pulp Composition*

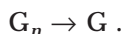
The pulp yield and composition of the raw material (Acetosolv-delignified *Eucalyptus* wood) used in this work, expressed in terms of weight percent (oven-dry basis), is summarised in Table II. In addition to the components shown in this table, the feedstock contains other fractions such as ashes, uronic acids, extractives and other compounds of minor importance, which were not determined.

TABLE II  
Pulp yield and composition of the Acetosolv pulp

Pulp yield, %	50.7
Composition	
Cellulose, %	79.0
Xylan, %	3.7
Residual lignin (expressed in terms of <i>kappa</i> number)	31.2
Acetyl groups, %	9.1
Acid-soluble lignin, %	0.5

### Cellulose Degradation During Deacetylation Treatment

The catalytic action of hydronium ions may result in cellulose hydrolysis giving glucose. Considering the kinetic models reported in literature<sup>14</sup> for the acid-catalysed hydrolysis of cellulose (here denoted  $G_n$ ), the experimental data for glucose (G) concentration were fitted to a pseudohomogeneous, first-order model according to the reaction:



Under the above hypothesis, the time course of the glucose concentration is given by:

$$C_G = C_{Gp} - (C_{Gp} - C_{G0}) \exp(-k_1 \tau) , \quad (1)$$

where  $C_{Gp}$  is the potential glucose concentration (corresponding to quantitative conversion of cellulose contained in pulp to glucose),  $C_{G0}$  is the glucose concentration at  $\tau = 0$ ,  $k_1$  is the first-order rate coefficient and  $\tau$  is the reaction time. Fitting the experimental glucose concentration profiles obtained at each temperature to Eq. (1) led to the values of  $k_1$  listed in Table III. Figure 1 shows the correspondence between experimental and calculated data at the several temperatures considered (160, 170, 180 and 190 °C). The limited

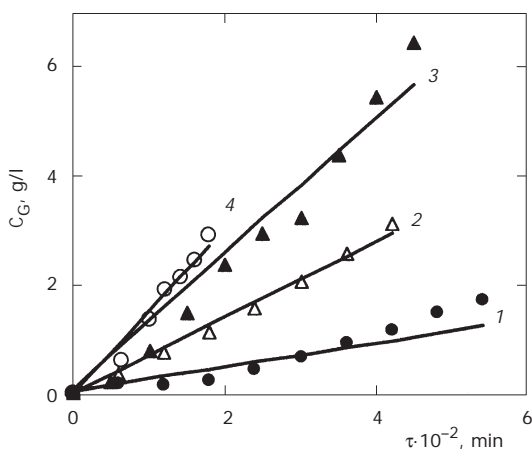


FIG. 1

Experimental and calculated glucose concentration profiles in treatment of hydrothermolysis carried out at indicated temperatures.  $t$ , °C: 1 160, 2 170, 3 180, 4 190

conversion of cellulose into glucose (a favourable feature of the aqueous treatments, which intend selective removal of acetyl groups and hemicelluloses from pulps) resulted in almost linear concentration profiles. Table IV lists the correlation coefficient ( $R^2$ ) and the mean relative quadratic deviation ( $\delta$ ) between the experimental and calculated data at all the temperatures considered. Material balances showed that the maximum cellulose conversion to glucose was 7.2%.

TABLE III  
Kinetic coefficients for cellulose, xylan and acetyl group degradation

$t, ^\circ\text{C}$	Kinetic coefficients, $\text{min}^{-1}$			
	$k_1 \cdot 10^5$	$k_2 \cdot 10^3$	$k_3 \cdot 10^3$	$k_4 \cdot 10^3$
160	2.00	2.32	2.84	2.41
170	6.42	4.29	5.71	3.15
180	11.6	6.10	9.63	4.71
190	13.8	12.5	15.2	5.65

TABLE IV  
Correlation coefficient ( $R^2$ ) and mean relative quadratic deviation between the experimental and calculated data ( $\delta$ ) for the glucose, xylose and acetyl group time series of data at all the temperatures considered

Statistical parameters	160 $^\circ\text{C}$		170 $^\circ\text{C}$		180 $^\circ\text{C}$		190 $^\circ\text{C}$	
	$R^2$	$\delta$	$R^2$	$\delta$	$R^2$	$\delta$	$R^2$	$\delta$
Glucose	0.9196	24.9	0.9886	9.1	0.9262	18.2	0.9669	14.3
Xylose	0.9889	3.4	0.9622	8.3	0.9616	11.4	0.9992	1.3
Acetyl group	0.9777	8.0	0.9865	8.0	0.9587	6.6	0.9544	10.6

### Xylan Degradation During Deacetylation Treatment

Xylan, a polymer made up of xylose units, is the main component of the hemicellulosic fraction of *Eucalyptus* wood, and the only hemicellulosic polymer present in significant amounts in Acetosolv-delignified pulps of this type of wood. Even though the processing of Acetosolv pulps in aqueous media has not been modelled in literature, various authors considered the aqueous hydrolysis of xylan contained in raw lignocellulosics<sup>9,15,16</sup>. Several hypotheses have been made in the formulation of kinetic mechanisms, including the possible presence of an unreactive – or slowly reactive – xylan fraction, the generation of xylooligosaccharides from xylan, the decomposition of xylooligosaccharides into xylose, and the decomposition of this sugar to give furfural and/or decomposition products. Owing to the higher catalyst availability in our case (derived from the high acetylation degree of pulps), the xylan degradation was modelled by two consecutive pseudo-homogeneous first-order reactions of xylan ( $X_n$ ) hydrolysis to xylose (X) and xylose decomposition into degradation products (DP):

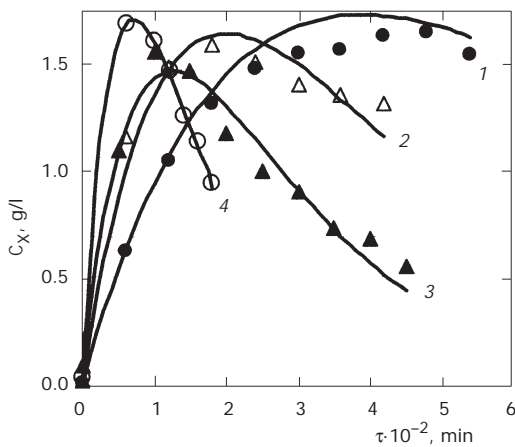
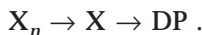


FIG. 2

Experimental and calculated xylose concentration profiles in treatment of hydrothermolysis carried out at indicated temperatures.  $t$ , °C: 1 160, 2 170, 3 180, 4 190

Considering that the concentration of degradation products is negligible at zero time, the equation for the time dependence of the xylose concentration can be calculated using the equation:

$$C_X = [(k_2/(k_3 - k_2))(C_{Xp} - C_{X0})[\exp(-k_2\tau) - \exp(-k_3\tau)] , \quad (2)$$

where  $C_{Xp}$  is the potential xylose concentration (corresponding to the quantitative conversion of the xylan contained in pulps into xylose),  $C_{X0}$  is the xylose concentration at  $\tau = 0$ ,  $k_2$  is the first-order rate coefficient for xylan degradation,  $k_3$  is the first-order rate coefficient for xylose decomposition and  $\tau$  is the reaction time. Fitting of the experimental xylose concentration profiles obtained at each temperature to Eq. (2) led to the values of  $k_2$  and  $k_3$  listed in Table III. Figure 2 shows the good agreement between experimental and calculated data of xylose concentration. Table IV shows the correlation coefficient ( $R^2$ ) and the mean relative quadratic deviation ( $\delta$ ) between the experimental and calculated data at all the temperatures considered. The maximum xylose concentration in liquors appeared at shorter reaction times when temperature was increased. The maximum experimental value (1.7 g xylose/l) was achieved after 60 min at the highest temperature used (190 °C).

Furfural was identified as the most important xylose degradation product. The furfural concentrations (expressed as g xylose equivalent/l) were in the range of 0.18–0.93 g/l at 160 °C, 0.04–1.35 g/l at 170 °C, 0.18–1.60 g/l at 180 °C and 0.11–1.51 at 190 °C. The lower furfural concentration achieved at 190 °C relative to 180 °C was ascribed to the increased participation of non-identified degradation products in the overall reaction scheme when operating at high temperatures as evident from material balances; this has been reported in literature<sup>15</sup>. Considering both the mechanism proposed for the xylan degradation and the experimental data obtained for the coefficient  $k_2$ , theoretical equations describing the time course of the xylan content in pulps can be derived (see below).

### *Study of Deacetylation*

Acetic acid (AcOH) is a by-product in lignocellulose hydrothermolysis<sup>17</sup> generated by the cleavage of acetyl groups substituents of polysaccharides. The modelling of acetyl group (Ac) hydrolysis was carried out assuming (as before) a pseudohomogeneous, first-order kinetics for the reaction





Assuming the above hypotheses, the time course of the acetic acid concentration is described by the equation:

$$C_{\text{AcOH}} = C_{\text{AcOHp}} - (C_{\text{AcOHp}} - C_{\text{AcOH0}}) \exp(-k_4\tau) , \quad (3)$$

where  $C_{\text{AcOHp}}$  is the potential acetic acid concentration (corresponding to the full conversion of the acetyl groups contained in pulps into acetic acid),  $C_{\text{AcOH0}}$  is the acetic acid concentration at  $\tau = 0$ ,  $k_4$  is the first-order rate coefficient for acetyl group degradation and  $\tau$  is the reaction time.

The acetic acid concentration profiles determined at all the temperatures assayed were well interpreted by Eq. (3), as can be seen in Fig. 3. Table IV lists the correlation coefficients ( $R^2$ ) and the mean relative quadratic deviations ( $\delta$ ) between the experimental and calculated data at all the temperatures considered. The concentration of acetic acid released from acetyl groups increased steadily with time and temperature, exceeding 8 g/l at all the temperatures used. Table III shows the values of the kinetic coefficient  $k_4$  determined under isothermal conditions. Considering the acetyl group content of the initial pulp, the liquor-to-solid ratio and the acetic acid con-

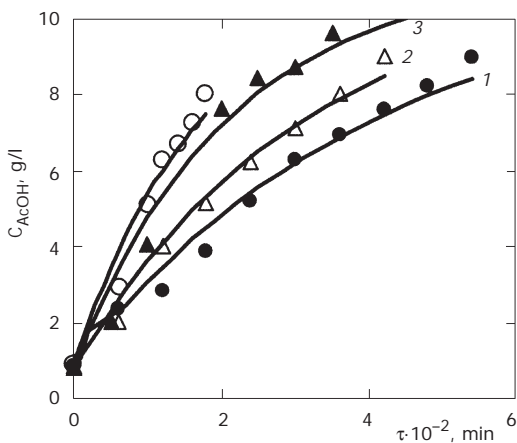


FIG. 3

Experimental and calculated acetic acid concentration profiles in treatment of hydrothermolysis carried out at the temperatures considered.  $t$ , °C: 1 160, 2 170, 3 180, 4 190

centration of liquors, it can be calculated that 69–94% of acetyl groups were cleaved at the end of treatment. These results confirm the ability of auto-hydrolysis to reduce the acetyl group content of pulps.

### Generalisation of the Kinetic Models

Assuming an Arrhenius-type dependence on temperature of the kinetic coefficients involved in the generation of glucose, xylose and acetic acid, it can be written

$$k_i = k_{0i} \exp [-E_{ai}/(RT)] , \quad (4)$$

where  $k_i$  ( $i = 1$  to 4) is the kinetic coefficient considered,  $k_{0i}$  is the corresponding preexponential factor,  $E_{ai}$  is the activation energy and  $T$  is the absolute temperature. The Arrhenius-type dependence of kinetic coefficients on temperature is confirmed by the linear relationship found between  $\ln k_i$  and  $1/T$  (see Fig. 4). Table V shows the values calculated for the regression parameters involved in Eq. (4), as well as the values of  $R^2$  and  $\delta$  obtained for each set of data.

Based on the results listed in Table V for preexponential factors and activation energies, the relationship between the pulp content of residual xylan (or residual acetyl groups) and the operational variables can be easily

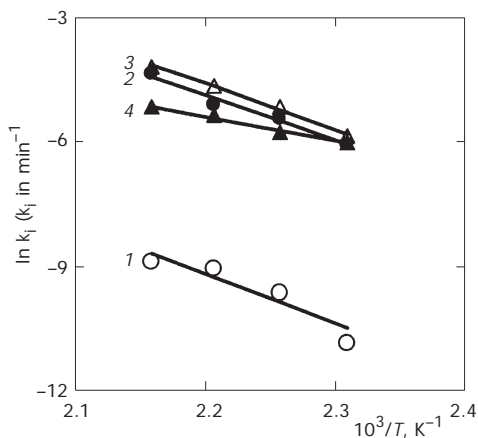


FIG. 4  
Arrhenius plots for kinetic coefficients  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$

calculated. Figures 5 and 6 show that xylan can be almost quantitatively removed from solid phase under severe conditions (temperature > 458 K, reaction time > 300 min), and that 80–90% of acetyl group removal can be expected under the same operational conditions.

TABLE V

Arrhenius parameters determined for the kinetic coefficients  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$  ( $k_{0i}$ , preexponential factors;  $E_{ai}$ , activation energies),  $R^2$  (correlation coefficient) and  $\delta$  (mean relative quadratic deviation)

Kinetic coefficients	$\ln k_{0i}$ ( $k_{0i}$ in $\text{min}^{-1}$ )	$E_{ai}$ kJ/mol	$R^2$	$\delta$
$k_1$	16.7	97.9	0.8864	1.9
$k_2$	18.9	90.0	0.9747	1.6
$k_3$	20.0	92.7	0.9904	1.0
$k_4$	7.7	49.4	0.9761	4.3

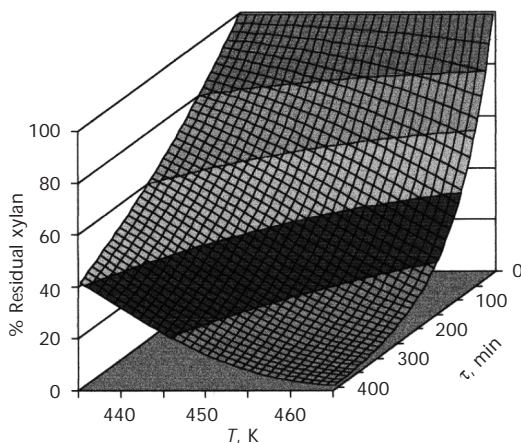


FIG. 5

Model predictions for the percentage of xylan remaining in pulp after treatment

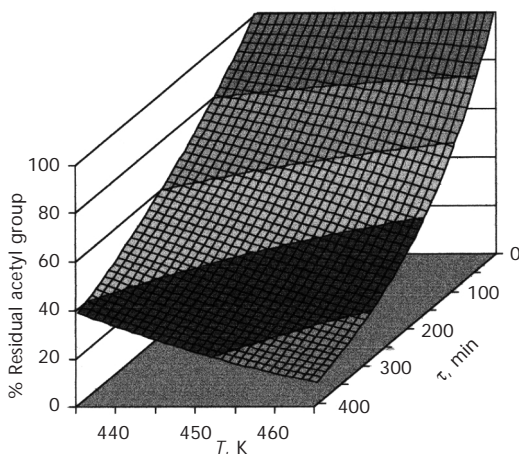


FIG. 6  
Model predictions for the percentage of acetyl groups remaining in pulp after treatment

## CONCLUSIONS

Treatment in aqueous media (hydrothermolysis) is useful for reducing both the xylan and the acetyl group content of the Acetosolv-delignified *Eucalyptus* pulps, leading to substrates with improved characteristics for bleaching.

The process was assessed using kinetic models based on pseudohomogeneous, first-order reactions for the degradation of cellulose to glucose, for the hydrolysis of xylan to xylose with further decomposition of this sugar, and for the cleavage of acetyl groups giving acetic acid. The kinetic coefficients, calculated for isothermal operation at the temperatures selected (160, 170, 180 or 190 °C), allowed a good interpretation of experimental data. The influence of temperature on the kinetic coefficients was established using Arrhenius equation, allowing the calculation of preexponential factors and activation energies for all the reactions involved. The generalised equations allowed the prediction of the xylan and acetyl group contents of pulps subjected to hydrothermal treatment under all the experimental conditions considered for the operational variables. Xylan can be almost quantitatively removed from the pulps by hydrothermal treatment carried out under harsh operational conditions, causing a simultaneous cleavage of more than 90% of initial acetyl groups. The scarce cellulose degradation (less than 7.2% of the initial cellulose was lost) was also a favourable feature of the considered process.

## SYMBOLS

$C$	concentration, $\text{g l}^{-1}$
$E_{ai}$	activation energies, $\text{kJ mol}^{-1}$
$k_1, k_2, k_3, k_4$	kinetic coefficients, $\text{min}^{-1}$
$k_{0i}$	preexponential factors, $\text{min}^{-1}$
$n$	number of measurements
$R^2$	correlation coefficient
$T$	absolute temperature, K
$t$	temperature, $^{\circ}\text{C}$
$\tau$	time, min
$\delta$	mean relative quadratic deviation defined as

$$\delta = \left[ \frac{1}{n} \sum_{i=1}^{i=n} \left( \frac{C_{\text{exp}} - C_{\text{calc}}}{C_{\text{calc}}} \right)_i^2 \right]^{1/2} \cdot 100, \%$$

## Subscripts

AcOH	acetic acid
calc	calculated
exp	experimental
G	glucose
p	potential
X	xylose
0	initial

The authors are grateful to the Ministry of Education of Spain for financial support of this work (project QUI99-0346). The authors wish to thank to Ms A. Ramos and Ms A. Rodríguez for their excellent technical assistance.

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