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Appendix A
Acidity Calculations

I. Calculation of Hydrogen Ion Concentration [H^+]

Basis:

100 kg OD wood

Given:

Concentration of added acid = CA (% H_2SO_4)

Liquid-to-solid ratio (L/S) = LS (kg/kg)

Neutralizing capacity of wood = EQW (eq/kg OD wood)

Neutralizing capacity of residue = EQR (eq/kg OD wood)

Then:

Cations neutralized = EQ = EQW - EQR (eq/kg OD wood)

Volume of solution = 100 x LS (liters, assuming a density of 1 g/ml)

Sum of sulfate and bisulfate in solution = SSS[1] = CA/9.8 (mols/L)

Cations in solution = CS[1] = EQ/LS (eq/L)

Sulfur Balance:*

$SSS = [HSO_4^-] + [SO_4^=]$

Charge Balance:

$CS = [HSO_4^-] + 2[SO_4^=] + [OH\text{-}] - [H^+]$

Equilibrium Constants:

$FKW = [H^+][OH^-]$

$FKA = [H^+][SO_4^=]/[HSO_4^-]$

The last four equations reduce to the cubic equation:

$A(1)[H^+]^3 + A(2)[H^+]^2 + A(3)[H^+] + A(4) = 0$

where

$A(1) = 1$

$A(2) = CS + FKA - SSS$

$A(3) = CS \times FKA - FKW - 2 \times SSS \times FKA$

$A(4) = - FKW \times FKA$

With numerical values for CS, SSS, FKW, and FKA, the coefficients may be evaluated and the cubic equation solved for its one real positive root which is the value of [H^+]. The values of FKA and FKW depend on temperature. At 25° C, they have the values 1.2×10^{-2} and 1.0×10^{-14}, respectively; at 170° C, 1.6×10^{-4} and 3.1×10^{-12}.

II. Calculation of Necessary Concentration of Added Acid to Obtain a Particular [H^+]

Basis:

100 kg OD wood

Given:

Liquid-to-solid ratio (L/S) = LS (kg/kg)

Hydrogen ion concentration = [H^+] (mols/L)

Neutralizing capacity of wood = EQW (eq/kg OD wood)

Neutralizing capacity of residue = EQR (eq/kg OD wood)

Then:

Cations neutralized = EQ = EQW – EQR (eq/kg OD wood)

Volume of solution = 100 x LS (liters, assuming a density of 1 g/ml)

Cations in solution = CS = EQ/LS (eq/L) assuming no $CaSO_4$ precipitation

Charge Balance:

$CS - [OH^-] + [H^+] = [HSO_4^-] + 2[SO_4^=]$

Equilibrium Constants:

$FKW = [OH^-][H^+]$

$FKA = [H^+][SO_4^=]/[HSO_4^-]$

From which,

$[SO_4^=] = (CS - FKW/[H^+] + [H^+])/([H+]/FKA + 2)$

$[HSO_4^-] = [SO_4^=][H^+]/FKA$

Thus,

$SSS = [SO_4^=] + [HSO_4^-]$, and $CA = 9.8 \times SSS$

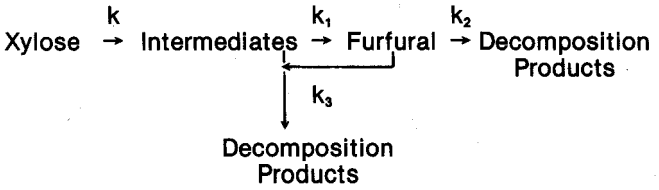
---

[1]It is possible that calcium ions, extracted from the wood, might precipitate as calcium sulfate. This would be a factor in calculating [H+], but it is difficult to bring in quantitatively. However, it was concluded that, at the conditions of prehydrolysis, precipitation would not occur because of the low concentration of sulfate ion. The secondary ionization constant for sulfuric acid decreases rapidly with temperature, and at 170° C and pH = 1.5, only about 0.5% of the acid is present as sulfate ion.

[2]Conventional concentration units of mols/L are used–i.e., [x] = concentration of x in mols/L.

Appendix B
Calculation of Furfural Yields During Xylan Hydrolysis

The differential production of furfural from xylose via the mechanism



was approximated by Root (1956) using the equation:

$$\frac{dF}{dt} = k \times (X - a \times F - b \times F \times X/XO)$$

where

t = time

k = reaction rate constant for xylose disappearance

X and F = molar concentrations of xylose and furfural

a = a(T,XO) (see Root 1956), where T = temperature

b = b(T,XO) (see Root 1956)

X0 = initial molar concentration of the xylose solution

The functions a and b were evaluated from experimental data, resulting in an excellent correlation. An integrated solution of the above equation was also presented, but only the differential form was used here.

Root's experimental procedure was to load small glass ampoules with solutions of various acid and xylose concentrations, react them at various temperatures for timed intervals, and measure the furfural yield. The quantity XO was a clearly defined, experimental variable included in the empirical correlation. In applying the correlation to the prehydrolysis, a problem arises as to the value to use for XO. The correlation is based on experiments in which the xylose concentration, initially XO, decreases exponentially with time. In the prehydrolysis, the xylose concentration is initially zero, rises to a maximum, and then decreases. Obviously, the relationship between the intermediate concentration and xylose concentration is very different from that present in Root's (1958) study.

Furfural production in the prehydrolysis was obtained by simultaneous numerical integration of the xylan removal rate curve, the xylose degradation rate equation, and the furfural rate equation above. The, furfural production rate, dF/dt, was evaluated at each instant in time by assuming two values for XO. One value used for XO was the actual xylose concentration at the moment; the second was the hypothetical xylose concentration assuming the total of all the xylose released up to that time to be present. Using these two values of XO, two values for each of a and b can be obtained. Thus, using all combinations of a and b, four values of dF/dt can be calculated. Of these four the minimum value was chosen.

Appendix C
Analysis of Glucose Reversion Data

The following procedure was used to extract values of the equilibrium constants, CD and CL, from the experimental data (table 10) obtained by the procedure described in the text. It was assumed that the system was at equilibrium (fig. 11) and thus:

$D = k_2G^2/k_3$

$L = k_4G/k_5$

where

D = disaccharide (mols/L)

L = levoglucosan (mols/L)

G = free glucose (mols/L)

Two values for the combined glucose can be obtained from the data (table 10):
1. Glucose after hydrolysis by the reducing method (col. 7) less the free glucose accompanying the reversion material (col. 4).
2. Glucose after hydrolysis by the oxidase method (col. 5) less (col. 4).
The average of these two values is the combined glucose or reversion material, CG:
CG = ((col. 7) + (col. 5) – 2 x (col. 4))/2 (mg/mL)
The total glucose, TG, is the sum of the free, G, and combined, CG, glucose:

TG = (col. 3) + CG (mg/ml)

The specific reducing power, RP, of the reversion material:

RP = ((col. 6) – (col. 4))/CG (mg glucose/mg combined glucose).

Assume that the reducing power of a mol of disaccharide is the same as that of a mol of glucose and that levoglucosan has no reducing power; then:

D = RP x CG/180 (mols/L)

and, since 2D + L = CG/180, then:

L = (1 – 2 x RP) x CG/180 (mols/L)

Thus the equilibrium constants, CD and CL, can be evaluated,

$CD = k_2/k_3 = D/G^2$ (L/mol)

$CL = k_4/k_5 = L/G$

where

G = free glucose

= (col. 3)/180 (mol/L)

The fraction of combined glucose present as levoglucosan is:

L/(2D + L) = (1 – 2 x RP)

Appendix D
Relationships Between Disappearance Rates of Reducing Power, Free Glucose, and Total Glucose

Define:

TG = total glucose (mol/L)

G = free glucose (mol/L)

D = disaccharide (mol/L)

L = levoglucosan (mol/L)

R = solution reducing power (mol glucose/L)

RPD = specific reducing power of disaccharide (mol glucose/mol disaccharide)

CD = disaccharide equilibrium constant

CL = levoglucosan equilibrium constant

Assume reversion equilibrium established, then:

$D = CD \times G^2$

L = CL x G, and

R = G + RPD x D

If RPD = 1.0, R = G + D

(dR/dt) = (dG/dt) + (dD/dt)

= (1 + 2 x CD x G) x (dG/dt)

TG = G + 2 x D + L
= G + 2 x CD x G^2 + CL x G

Thus, G = (-B + SQ)/2

where

B = (1 + CL)/(2 x CD), and

$SQ = \sqrt{B \times B + 2 \times TG/CD}$

(dG/dt) = (d(SQ)/dt)/2

= (d(TG)/dt)/(2 x CD x SQ)

(dR/dt) = (1 + CD x (-B + SQ)) x (dG/dt)
= (1 + CD x (-B x SQ)) x (d(TG)/dt)/(2 x CD x SQ)

Define:

F1 = 1 + CD x(-B + SQ)

F2 = F1/(2 x CD x SQ)

Then:

(dR/dt) = F1 x (dG/dt)
= F2 x (d(TG)/dt)

The function F1 increases from 1.0 to 1.10, and F2 decreases from 0.90 to 0.84 as the total concentration changes from 0 to 20% glucose.

Appendix E
Calculation of Glucose Yields (From Fig. 16)

Basis:
100 g lignocellulose (LC)

Define:

G = free glucose (mol/L)

L = levoglucosan (mol/L)

D = disaccharides (mol/L)

TG = total glucose, free + combined

= G + 2 x D + L (mol/L)

R = reducing power of solution

= G + D (mol/L)

v = volume of hydrolyzing solution at 25° C (L)

t = time (min)

FKC = cellulose weight loss rate constant (min^{-1})

FKR = reducing power rate constant (min^{-1})

Given:
Total cellulose in lignocellulose = CL (%)

Cellulose resistant to hydrolysis = CR (% of total cellulose)

Liquid-solid ratio = LS (kg/kg OD lignocellulose)

Concentration of added acid = CA (%)

Temperature = T (°C)

Neutralizing capacity of lignocellulose = EQW (eq/kg OD lignocellulose)

Neutralizing capacity of hydrolyzed residue = EQR (eq/kg OD lignocellulose)

Equilibrium constant for disaccharides;
$D = CD \times G^2 = CD$

Equilibrium constant for levoglucosan; L = CLxG = CL

Numerically integrate:

$$d(TG)/dt = FKC \times CL \times CR \times \exp(-FKC \times t)/(16200 \times V) - FKR \times R/F2 \quad (E1)$$

$$(TG)_{t=0} = CLx(100 - CR)/(16200 \times VO) \quad (E2)$$

Equation (El) assumes that k_1 and $k_2 >> kg$ (fig. 16) and that L and D are in complete equilibrium with G. It is also assumed that the easily hydrolyzed cellulose is instantaneously converted to glucose giving the boundary condition of eq. (E2). VO is the volume of the solution (associated with 100 g of lignocellulose) containing this amount of glucose-that is, the glucose liberated from the easily hydrolyzed cellulose.

The first term on the right of eq. (E1) is the production of total glucose from the resistant cellulose; the second term is the destruction of total glucose. The rate constant for cellulose hydrolysis is calculated from the equation:

$$FKC = 2.80 \times 10^{20} \times (CH)^{1.218} \times \exp(-21600/(T + 273.1)) \quad (E3)$$

Here CH is the H-ion molarity of the solution after neutralization of the ash constituents but before release of the easily hydrolyzable cellulose. It is calculated by the procedure in Appendix A using the given values of CA, LS, EQW, and EQR. Consistent with the handling of the experimental data on which eq. (E3) is based, CH does not vary as the reaction proceeds and thus, at isothermal conditions, FKC has a constant value.

The volumetric factor, V, is a function only of glucose concentration and does not vary with temperature. The volume of the reacting solution does vary with temperature, but this effect is implicitly included in the correlation of the rate constant, FKC, and the equilibrium constants, CD and CL. The factor V varies throughout the reaction period and is related to TG through the density (DEN, g/L) by:

$$V = LSx\ 100/(DEN \times 1000 - GT \times 180) \quad (E4)$$

The solution densities are assumed to be those of glucose solutions of the same concentration at an ambient temperature of 20° C. Thus eq. (E4) expresses V as a function of TG.

The second term on the left of eq. (E1) accounts for the disappearance of total glucose, TG, from the solution. The relationship between the differentials for R and TG has been shown to be:

$$d(TG)/dt = (dR/dt)/F2 \quad (E5)$$

and since dR/dt = FKR x R, the rate of total glucose disappearance, the second term, on the left of eq. (E1), is FKR x R/F2. Each of the factors FKR, R, and F2 is related to TG:

R is the reducing power of the solution-that is, R = G + D. It is converted to a function of TG as shown in Appendix D. Using that nomenclature:

$$R = G + CD \times G^2 \quad (E6)$$

and

$$G = (-B + SQ)/2 \quad \text{(E7)}$$

F2 is related to TG by the expression derived from Appendix D:

$$F2 = (1 + CD \times (-B + SQ))/(2 \times CD \times SQ)$$

The parameters CD and CL are assumed to be exponential functions of temperature, the expressions having been derived from reversion data taken at 180° and 230° C:

$$CD = 1.127 \times 10^{-5} \times \exp(4272/(T + 273.1)) \quad \text{(E8)}$$

$$CL = 4.758 \times 10^{4} \times \exp(-6471/(T + 273.1)) \quad \text{(E9)}$$

FKR, the rate constant for the disappearance of reducing power, is obtained from McKibbins' correlation (1958). The inputs required are T, acid normality (N), and glucose concentration. The glucose concentration is assumed to be GT. The acid normality varies with the solution volume which, as described above, is dependent on GT. It is determined as follows.

The initial acid normality is established from CH, the H-ion molarity used above to calculate FKC. This molarity corresponds to a particular sulfuric acid normality, which may be determined from CH by the procedure given in Appendix A, assuming EQ = O. However, at the pH level considered here, it can be assumed that only the first hydrogen on sulfuric acid is effective and the initial normality, prior to any hydrolysis, is simply twice the H-ion molarity. The normality throughout the reaction is inversely related to the volume change, and thus to TG by the equation:

$$N = 2 \times CH \times (DEN \times 1000 - GT \times 180)/1000 \quad \text{(E10)}$$

It is assumed in eq. (E10) that the density of water at ambient temperature is 1 g/cm^3.

With all its parameters related to TG, the differential eq. (E1) with its boundary condition can be numerically integrated to obtain TG as a function of time. This is most readily done using concentration units of mol/L and subsequently using the volumetric relationships, converting to percentage yields.

Appendix F
Comparison of Ethanol Yields from Percolation and Two-Stage Processes

Estimation of Saccharification Efficiency by Percolation

We can suppose that Douglas-fir, with a composition of 45% glucan and 10.8% mannan, gives an ethanol yield of 260 L of 190-proof alcohol/tonne of OD wood (Lloyd and Harris 1955).

The potential sugars from a tonne of wood are glucose (500 kg) and mannose (120 kg). The yield of glucose from the resistant cellulose is calculated as illustrated in figure F1. Of the potential 120 kg of mannose, it is assumed that 90% will end up in the product solutions. It will be primarily in the hemicellulose stream and some will be in the glucose-rich stream; but 90%, or 108 kg of mannose, is considered as available for fermentation. Of the potential glucose, 37.5 kg (7.5%) is from readily hydrolyzable cellulose, and it is supposed that 7.0% is recovered as fermentable sugar in the hemicellulose stream. These sugars, which are not from the resistant cellulose, will yield 90.8 L of ethanol. The remaining 169.2 L of ethanol must come from the resistant cellulose, which has a glucose equivalent of 462.5 kg. Consequently, conversion of the resistant cellulose to glucose must occur in 57.6% yield.

Yields from Percolation Processing of Southern Red Oak

The wood composition presumed as the basis for the percolation process is that given in table 1 (sample 3) and the same as that used in the first process calculations.. One tonne of this material contains 184 kg of xylan, equivalent to 209 kg of xylose, and 378 kg of glucan, equivalent to 420 kg of glucose (fig. F2). It is assumed that 80% of the xylose will be recovered in the hemicellulose fraction. Unlike mannose, the xylose released during the resistant cellulose hydrolysis will be largely destroyed. The hemicellulose cut will contain 7.5% of glucose originating from the readily hydrolyzable cellulose.

This is not the only glucose accompanying the xylose fraction. Because of poor fractionation of the components, some of the glucose obtained from hydrolysis of the resistant cellulose will be washed out with the hemicellulose-derived sugars. It was assumed that the glucose content of the hemicellulose stream would be twice that obtained with perfect separation. The remaining glucose available for fermentation yields 124 L of ethanol.

Yields from Two-Stage Processing of Southern Red Oak

The yields indicated (fig. F3) are those previously established in the text for two-stage processing of southern red oak.

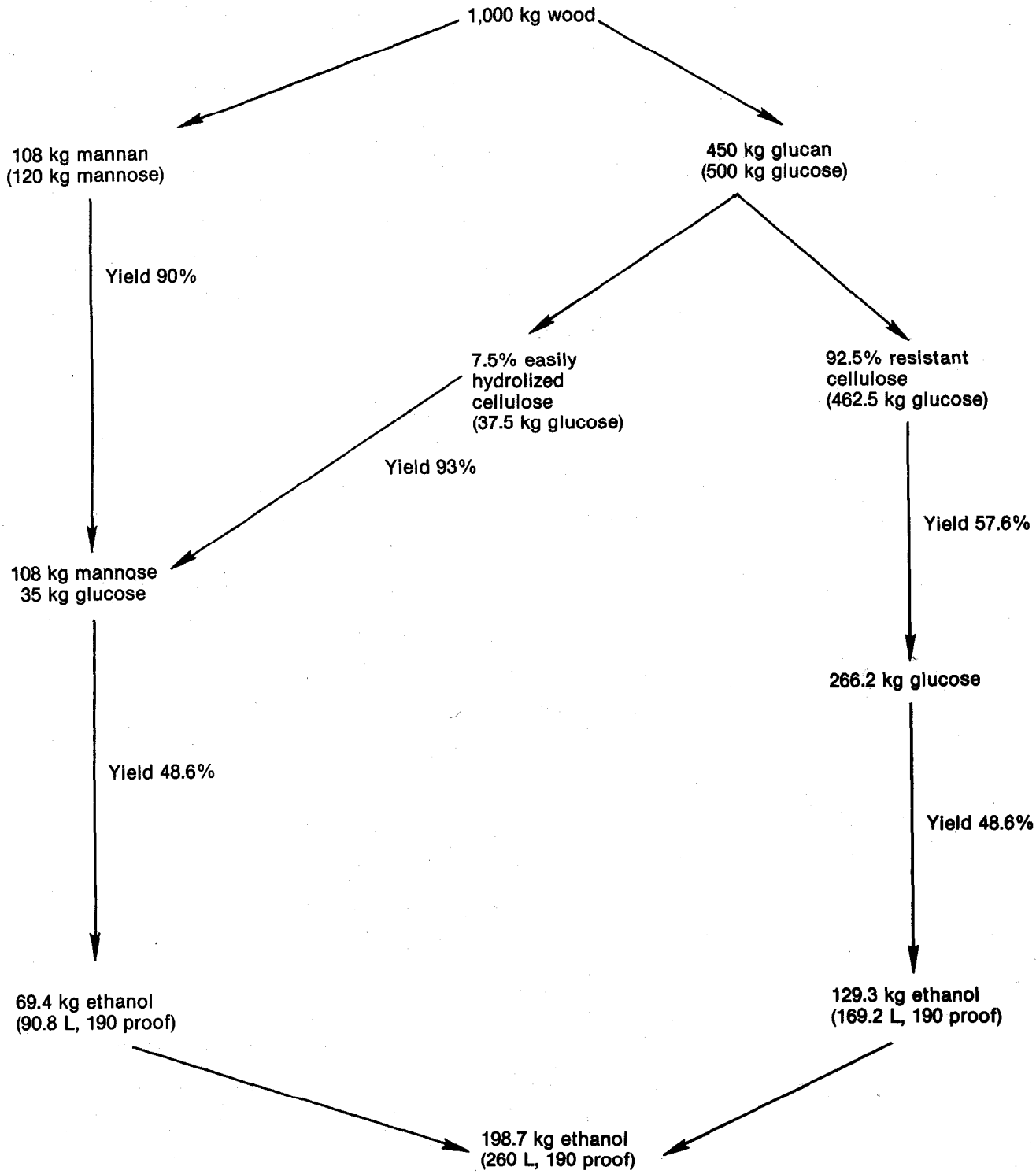


Figure F1.—Estimation of saccharification efficiency in the percolation process.

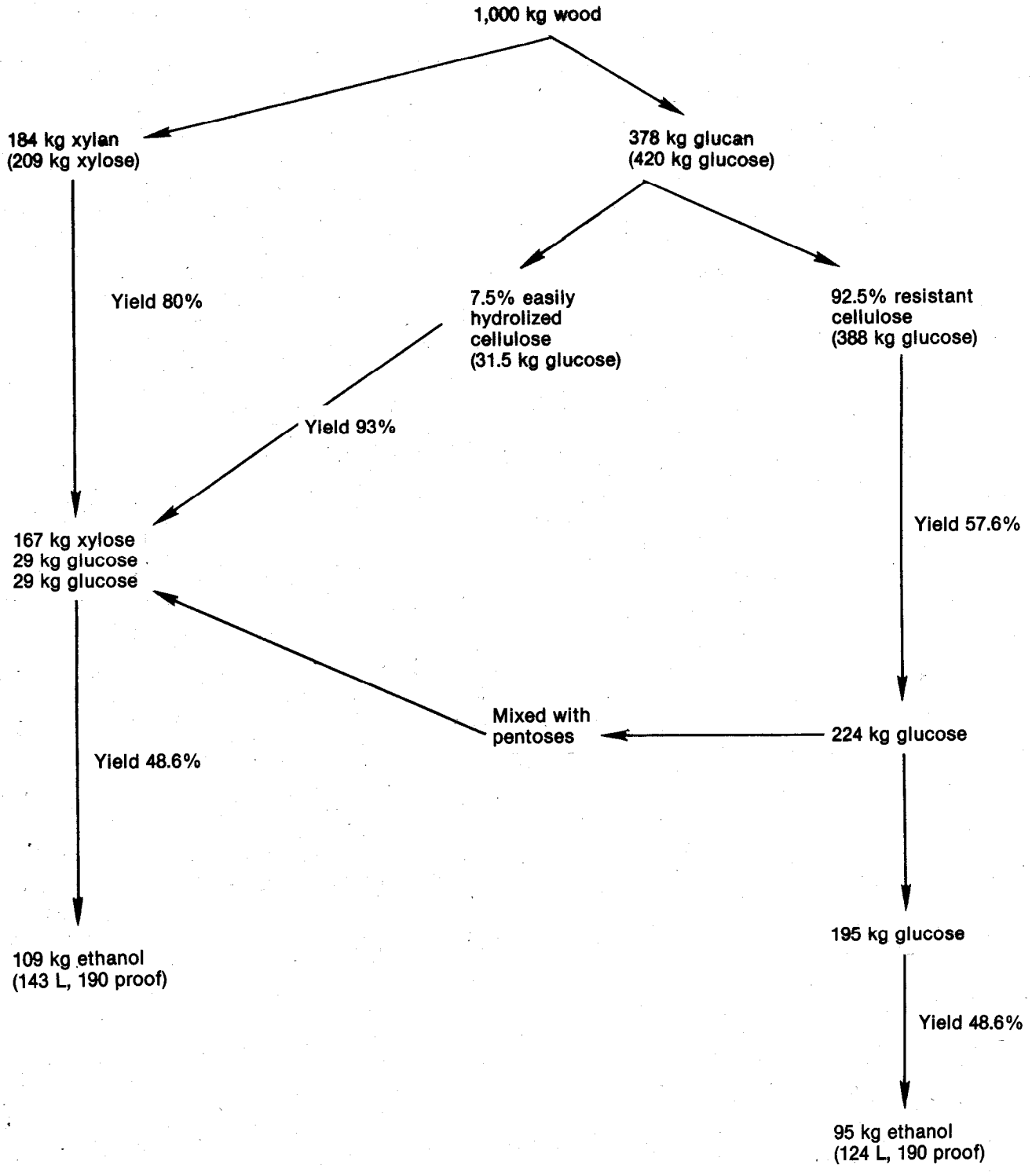


Figure F2.—Percolation processing of southern red oak.

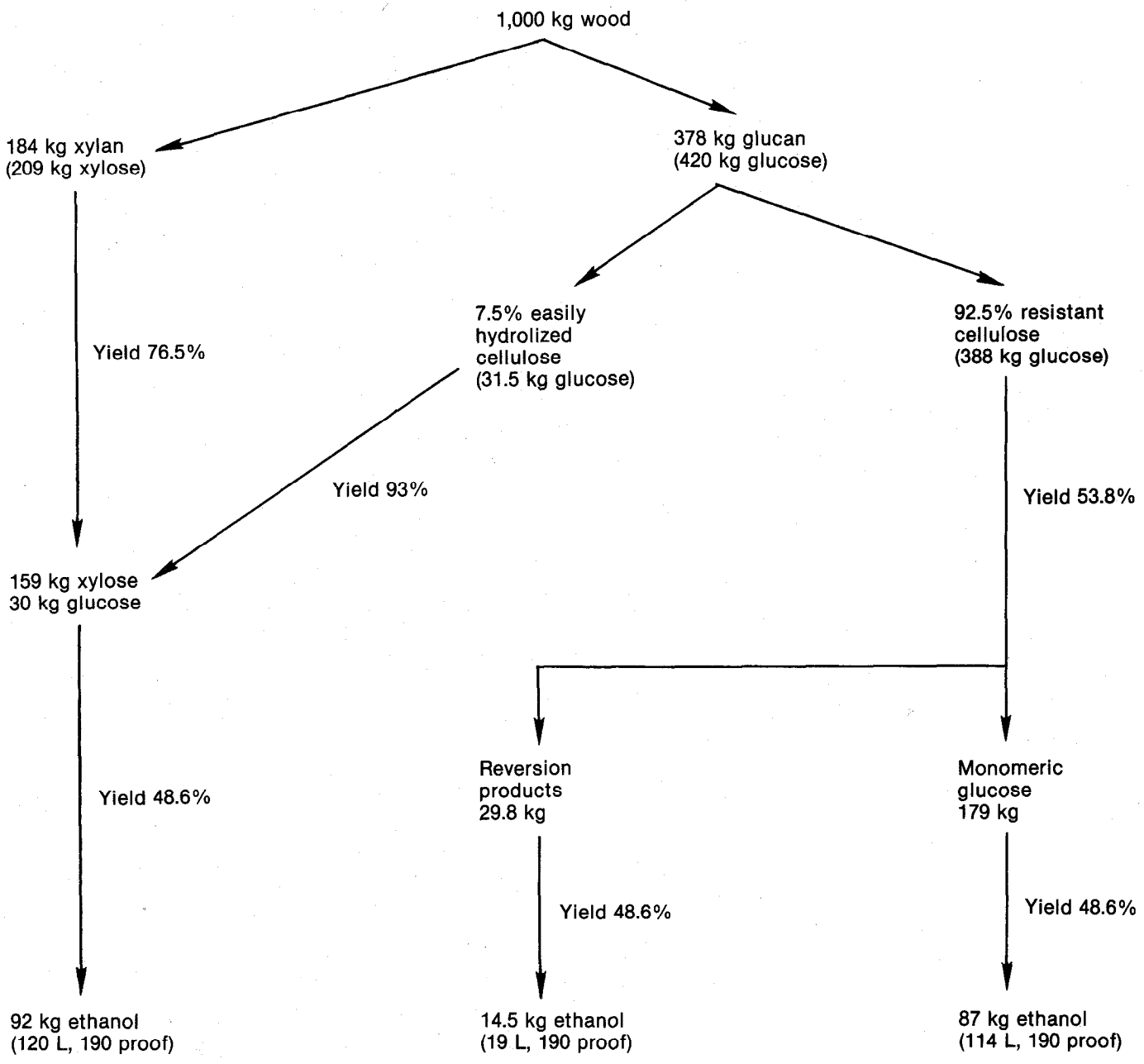


Figure F3.—Two-stage processing of southern red oak.

Appendix G
Experimental and Chemical Analysis Procedures

This section briefly describes some of the experimental methods used in this report and gives access to sources containing more detailed information.

1. Ampoule kinetic technique.

The ampoule kinetic technique refers to the use of sealed glass ampoules to study chemical reactions. It is a simple, very accurate, efficient procedure for the systematic study of homogeneous liquid reactions and heterogeneous liquid-solid reactions.

For homogeneous reactions, 130-mm lengths of 1- or 3-mm glass tubing are quantitatively loaded with liquid by a special syringe. The loaded tubes are sealed under vacuum. The smaller-diameter reactors contain as little as 0.025 mL of solution. The heterogeneous reactions use 130-mm lengths of 3- or 5-mm tubing. If the substrate is wood, it is cut into small disks by special tools. The disks are normally cut perpendicular to the longitudinal axis of the wood and are thin enough (~0.25 mm) so that the lumens of all the cells are open. Usually samples of 0.25-0.5 g are used.

The loaded ampoules are heated in an oil or molten salt bath equipped with stirrers and temperature controllers. A temperature of 300° ± 0.5° C can be maintained in the molten salt bath. Elaborate precautions are taken to eliminate drafts and other factors causing nonuniform temperature throughout the baths. The baths have auxiliary quench tanks, and samples can be transferred quickly from the high-temperature zone to the quench liquid. The time of immersion is automatically recorded. The baths are provided with safety shields that allow remote manipulation of reactors. Large numbers of samples can be accommodated.

The strength and heat-transfer characteristics of the glass ampoules have been studied.[1,2] The l-mm-diameter ampoules are safer and heat up more quickly than the larger ones. These small reactors can withstand pressures of 8,500 kPa. Procedures and equipment employed with homogeneous reactions can be found in publications by McKibbins (1958) and Root (1956) and those for heterogeneous reactions in a thesis by Springer (1961).

2. Lignocellulose and wood analyses.

a. Extractives-Wood containing tannins, such as southern red oak, require extraction with ethanol-benzene followed by extraction with ethanol (TAPPI Standard T12 (1982)). This analysis was done only on wood samples.

b. Ash-The TAPPI Standard T211 OM-80 (1982), which is similar to the ASTM Standard D 1102-56 (1981), was used.

c. Lignin-When wood Is treated with concentrated sulfuric acid, (72%) the carbohydrates are solubilized; the insoluble residue, measured gravimetrically, is reported as lignin, often referred to as Klason lignin. This value may be somewhat less than the actual lignin content since some lignin may be acid soluble. In the case of oak wood, the sample must be extractive free. The procedure used, described by Saeman et al. (1954), is similar to TAPPI Standard T222 (1982).

d. Carbohydrates-Two basically different procedures were used to analyze for carbohydrates. In one, the wood or lignocellulose sample Is reacted In strong sulfuric acid under conditions suitable for dehydration to furans. The amounts of the various furans are determined spectrophotometrically and the carbohydrate content calculated by the use of standards. Carbohydrates In solution may also be determined by this method. Although glucose and mannose (also xylose and uronic anhydride) react to form the same furan, they may be determined separately by reacting the sample in sulfuric acid containing different additives. Solid or liquid samples may be analyzed for glucose, mannose, xylose, and uronic anhydride. Galactose, if present, is reported with glucose and arabinose with xylose.. This procedure, described by Scott (1976; 1979) and Scott et al. (1974), was used for all samples Involved in the digester studies.

In the second procedure, the carbohydrates of the lignocellulose are solubilized with strong sulfuric acid and converted to solutions of monomeric sugars as described by Saeman et al. (1954). The solutions are then analyzed for the component sugars using, paper or liquid chromatography. The preparation of solutions and the quantitative paper chromatographic procedures are completely described in the ASTM Standard D 1915-63 (1981). Depending on the eluting solvent used, analysis is for either three or five sugars. When only three sugars-glucose, mannose, and xylose-are reported, the galactose is included with the glucose and arabinose with the mannose. The liquid chromatographic procedure employed does not require prior reaction of the sugars. The particular method developed at this laboratory (Pettersen et al. 1984) Is based on previous work by Wentz et al. (1982) and Paice et al. (1982).

In addition to the dehydration procedure mentioned above, wood samples were sometimes analyzed for uronic anhydride by a more conventional procedure (Browning 1949). This method relies on the quantitative liberation of CO, induced by refluxing in 12% hydrochloric acid.

[1]Tomlin, R.; Baumgartner, J. Strength and heat transfer tests of glass tubing reactors. Madison, WI: U.S. Forest Service, Forest Products Laboratory; May 1956. 7 p. Unpublished report.

[2]Wasser, R. B. Heat transfer tests of glass tubing reactors. Madison, WI: U.S. Forest Service, Forest Products Laboratory; Dec. 1957. 6 p. Unpublished report.

e. Acetyl–Two procedures were used for acetyl determination. One was similar to a method reported by Wiesenberger (1947). The acetyl groups are released by hydrolysis in alkaline medium; the solution is then acidified and acetic acid removed by steam stripping. The amount of isolated acid is determined by titration.

In the second procedure, the acetyl groups are hydrolyzed in the same manner as above, but the acetic acid released is assayed by gas chromatography. For this, a Supelco 60/80 Carbopak C/0.3% carbowax 20 M/0.1% H_3PO_4 column (Supelco, Inc., Bellefonte, Pa.) was used at the conditions recommended by the manufacturer. The quantity of acetic acid was determined with an internal standard of propionic acid.

3. Solution components analyses.

a. Carbohydrates-In addition to the applicable procedures discussed in the preceding section for solids, two others should be noted:

A Beckman Glucose Oxidase Analyzer (Beckman Instruments, Inc., Fullerton, Calif.) was used without modification of the recommended procedure, to determine monomeric glucose.

The Schaffer-Somogyi volumetric procedure (1933) or Nelson's calorimetric modification of Somogyi's method (1944) was used to measure the reducing power of solutions. These methods were used for solutions containing a single sugar but were also valuable for determining the amounts of oligomers in solution. This was done by measuring the increase in reducing power resulting from mild acidic hydrolysis of the sample.

b. Other components–Components were considered in two groups:

Acetic, formic, and levulinic acids-These acids were determined by high-performance liquid chromatography using a Bio-Rad HPX-87H column (Bio-Rad Laboratories, Richmond, Calif.) following the supplier's recommended operating conditions. This was the only analysis used for formic and levulinic acids, but most acetic acid samples were analyzed by the method used for acetyl.

Furfural and hydroxymethylfurfural–These compounds can be separated from other components of hydrolysates using the same HPLC procedure as used for the above acids. The few HMF analyses reported were obtained in this way. However, furfural measurements were obtained by the distillation procedure developed by Root (1956).

The Forest Products Laboratory (USDA Forest Service) has served as the national center for wood utilization research since 1910. The Laboratory, on the University of Wisconsin-Madison campus, has achieved worldwide recognition for its contribution to the knowledge and better use of wood.

Early research at the Laboratory helped establish U.S. industries that produce pulp and paper, lumber, structural beams; plywood, particleboard and wood furniture, and other wood products. Studies now in progress provide a basis for more effective management and use of our timber resource by answering critical questions on its basic characteristics and on its conversion for use in a variety of consumer applications.

Unanswered questions remain and new ones will arise because of changes in the timber resource and increased use of wood products. As we approach the 21st Century, scientists at the Forest Products Laboratory will continue to meet the challenge posed by these questions.