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## An Operation Research Approach to the Economic Optimization of Kraft Pulping

Robert E. Packwood  
*Western Michigan University*

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AN OPERATIONS RESEARCH APPROACH TO  
THE ECONOMIC OPTIMIZATION  
OF KRAFT PULPING

by

Robert E. Packwood

A Thesis submitted to the  
Faculty of the Department of Paper Technology  
in partial fulfillment  
of the  
Degree of Bachelor of Science

Western Michigan University

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## ABSTRACT

The first attempt to apply operations research to the kraft industry came in 1959 by C. W. Carroll at the Institute of Paper Chemistry. Carroll developed a pulping rate expression and incorporated engineering balances to complete his mathematical model. Carroll then developed an optimization technique to optimize kraft mill economic performance.

This work develops the mathematical model utilizing a different pulping rate expression and further develops certain areas (e.g. recovery boiler, lime kiln, and washer models) utilizing regression equations obtained from literature and material and energy balances in an approach much like that of Boyle and Tobias.

An attempt was made to incorporate automatic step size reduction into Carroll's optimization method (Created Response Surface Technique). A comparison of a three-dimensional optimization output with that of Carroll's user-response program is included.

Results of the optimization comparison indicated that it is possible to incorporate automatic step size reduction and obtain better accuracy than Carroll reported. However, results indicate that it may be desirable to use the CRST to get close to the optimum and then use another technique to pinpoint the final optimum.

Comments on the Industrial Applicability of this approach are included.

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## INTRODUCTION AND HISTORICAL BACKGROUND

The expectation of profit is the economic driving force motivating business activity in a free-enterprise economy. Profit may be maximized in the short run by maximizing net return and in the long run by maximizing return on investment. In either case this may involve a need for more efficient production, and, as a result, techniques have been developed to find optimal solutions of industrial process problems.

Operations Research (O.R.) developed during World War II when allied powers hired large numbers of scientists and engineers to solve complex military problems. Upon conclusion of the war, what had become known as "Operations Research" in the military was found to be well suited for peace time industrial problems.

Carroll (1), in a pioneering effort, outlined the O.R. approach and applied it to the kraft pulping process. His work involved developing a mathematical model of a pulp mill, determining restraints on each of the independent variables, developing an iterative maximization technique called The Created Response Surface Technique (CRST), and applying it to the mathematical model to find the optimum process parameters with respect to net dollar return.

Carroll's mathematical model was derived from development of a pulping rate expression and energy and material balances around the process.

### Carroll's Restrictions

Boyle and Tobias (2), noted the restrictions of Carroll's work: the independent variables of the model did not coincide with plant process

variables and some key parameters (e.g. recovery furnace sulfur losses) were taken on assumption. Boyle and Tobias went on to incorporate a quantitative approach to kraft cooking suggested by Hinrichs (3) and reformulate the process model. Some process parameters (e.g. chemical losses) still were not described in terms of manipulated process variables.

### Pulping Rate Expression

In developing his rate expression, Carroll assumed hydroxide to be the rate limiting constituent since, he reasoned,  $\text{Na}_2\text{S}$  would hydrolyze to  $\text{NaSH}$  which would further hydrolyze to  $\text{H}_2\text{S}$  and  $\text{NaOH}$ . The final rate expression considered the influence of active alkali, time up to temperature, cooking temperature, liquor:wood ratio, lignin content of the wood, as well as the average chemical concentration throughout the cook.

Vroom's classical work (4) on the H-Factor approach to pulping kinetics (rate of reaction as a function of temperature) provides the basis for many cooking control systems in use today.

Ringley (7) investigated the H-Factor and found that the relative rate of reaction was calculated using the bulk delignification rate activation energy. His study indicated that the reaction terminated in the residual delignification rate area when cooking loblolly pine chips. Using the average activation energy for kraft pulping given by Rydholm (37), Ringley recalculated the H-Factor and found it compared closely with his results.

Hinrichs (3) investigated the effective cooking time to a given K number as a function of other cooking variables. Effective alkali was found to determine the degree of cooking possible in a kraft cook, confirming reports by Hart and Strapp (5), and Rengfors and Stockman (6). Hinrichs found that for any effective alkali usage, there was a sharply defined minimum K number that could be obtained.

Boyle and Tobias (2) later used effective alkali, sulfide on wood, and liquor:wood ratio as suggested by Hinrichs but used them in linear fashion with restrictions of being accurate only within small ranges of the conditions for which the coefficients were determined.

Hatton, Keays, and Hejjas (8) in a study of Western Hemlock developed the E-Factor, which defines the total energy input of the pulping system. This E-Factor can be thought of as a three-dimensional version of the two-dimensional H-Factor where  $E = H$  (Effective Alkali).

Lemon and Teder (13) pointed out that hydroxide and hydrogen sulfide ( $HS^-$ ) ions are usually assumed to be the delignifying agents. Their concentrations are overestimated by using the concentrations of effective alkali and total sulfide sulfur. Only when the equilibrium constant,  $K_b$  ( $K_b = \frac{[HS^-][OH^-]}{[S^{2-}]}$ ), can be assumed infinite will the effective alkali equal  $HS^-$ . The difference becomes more pronounced as the value of the equilibrium constant becomes lower. Lemon and Teder arrived at a rate equation of the form:

$$r = k_1 [OH^-] + k_2 [OH^-] [HS^-]$$

Edwards and Norberg (14) developed a further extension of the H-Factor for pulping called the  $\tau$  factor. Using the H-Factor concept, they reduced the number of independent variables in kraft cooking from five (liquor:wood ratio, effective alkali, sulfidity, time, and temperature) to just one (the  $\tau$  factor), provided that alkali to the digester is not undercharged.

More recent work by Edwards, Norberg, and Teder (15) involved fitting a rate equation of the form:

$$= (k_1 + k_2 [S(-II)]^a [OH^-]^b (L - L_f))$$

where  $[S(-II)] = [HS^-] [S^{2-}]$

L = remaining lignin

$L_f$  = lowest attainable lignin content

Chari (16), in developing a model for batch digester control, found that under particular mill conditions active alkali correlated fairly well with effective alkali. Because of this correlation as well as the familiarity of the operators with active alkali analysis, it was decided to use active alkali concentrations in the mathematical model. The final model equation was:

$$P = \frac{5,711 D_o^{.2144}}{Q_o^{.913} H^{0.399}} \text{ where}$$

P = Permanganate No.  
 $D_o$  = Liquor:wood ratio  
 $Q_o$  = Active Alkali  
H = H-Factor

Yield was predicted as follows:

$$Y = 19.43 + 0.73P \quad \text{for } 46 \leq P \leq 30$$

Utilization of the above model in dedicated computer control reduced Permanganate No. standard deviation to 0.98.



### Pulp Washing

To handle chemical loss in pulp to the screen room Carroll obtained a dilution curve for a hypothetical multistage washer and determined its equation. This equation calculates chemical loss as a function of the ratio lb. wash water per ton air-dried pulp. Included also is the calculation of defoamer cost in screening.

### Evaporation

To arrive at an evaporation model Carroll obtained evaporation performance data on a conventional six-effect arrangement. Carroll then formulated regression equations for steam economy, cost, and evaporation rates as a function of solids input to the evaporators and load on the evaporators. Solids leaving the evaporators was assumed constant at 52%.

Boyle and Tobias left the evaporator steam economy as an input variable in the kraft mill simulation program.

There are many unit operations texts (18) available which are useful in modeling steam economy, costs, and evaporation rates as a function not only of load on the evaporators and solids content of the evaporator feed but also solids content of liquor leaving the evaporators.

### Black Liquor Oxidation

There is much literature available on various low odor recovery boiler systems (24, 25, 26, 27, 28, 30, 31 and 32). At least at the present time many mills are operating with cascade evaporation of oxidized black liquor.

Padfield (29) reported on Champion's Pasadena Mill oxidation system expansion. Data is given on the effect of sulfidity on  $\text{SO}_2$  emission from the recovery furnace.

Murray and Rayner (33) studied  $\text{H}_2\text{S}$  emission during direct contact evaporation. It was found that a direct-contact evaporator may emit hydrogen sulfide or may absorb hydrogen sulfide (and  $\text{SO}_2$ ) from the flue gases, depending upon conditions in the liquor and in the incoming gas stream. Emission of hydrogen sulfide is favored by high concentrations of sodium sulfide and low pH levels in the liquor, and by low concentrations of hydrogen sulfide in the entering flue gas. Absorption of hydrogen sulfide from the incoming flue gases was observed in all cases regardless of pH when the sodium sulfide concentration in the black liquor was reduced to zero by oxidation.

Murray (34) has studied the kinetics of black liquor oxidation. He reported the rate of oxidation of weak black liquor varied in a complex manner depending upon the partial pressure of oxygen, the sodium sulfide concentration, the rate of liquor stirring, and the chemical reaction taking place under the prevailing experimental conditions. Equations were developed to describe the oxidation rate in terms of sulfide concentration and oxygen pressure. Data on rates obtained in the laboratory apparatus are compared with results obtained from studies of pilot plant and full-scale oxidation units.

Morgan and Murray (35) showed the oxidation to thiosulfate to be the product of sequential reactions. Sulfide concentration in the black liquor pH of the black liquor, and hydrogen sulfide concentration in the

flue gas was shown to determine the mass transfer of hydrogen sulfide between the black liquor and flue gases, as the gases pass through the direct contact evaporator. A two-fold increase in airflow was found to yield a rate increase of 40-50%. Oxidation rate was found to decrease with increased retention time (increased liquor height in tower). Oxidation rate also was found to decrease with increased sulfide concentrations. It was deduced that the overall rate is dependent upon the amount of sulfide in the reactor.

Christie and Stubar (36) undertook a study to determine the important criteria in black liquor oxidation tower design. Data was presented from which a regression model may be drawn.

### Burning

To obtain recovery furnace burning relations Carroll chose a black liquor solids analysis typical of what Combustion Engineering, Inc. (19) had encountered. He assumed 94% of total sulfur is retained as  $\text{Na}_2\text{SO}_4$  and remaining Na is present as  $\text{Na}_2\text{CO}_3$  before reduction. A constant reduction of 95% is also assumed. Flue gas composition is calculated from the balance as well as smelt composition.

Tobias and Boyle, in constructing their computer program, treated the burning relations much the same in that the furnace reduction efficiency and total sulfur loss are left for user input.

Borg and Warnqvist (20) developed a mathematical model of sulfur emission from "soda-house" units. Sulfur emission in the form of  $\text{SO}_2$  was assumed much greater than sulfur in the form of  $\text{H}_2\text{S}$ . Emission was studied in two regions of the furnace; the bed region, and the liquor

spray region. Particulate emission ( $\text{Na}_2\text{SO}_4$ ) and fume emission ( $\text{SO}_2$ ) were distinguished from each other. It was found that  $\text{SO}_2$  emission for a given sulfidity decreased with increased liquor solids content (due to calorific increase). At the higher calorific values, and the resultant higher furnace temperatures, increased sodium emission ( $\text{Na}_2\text{SO}_4$ ) was found also.

Bhada, Lange, and Markant (22) reported on the effect of operational variables on air pollution from kraft recovery units. The effects of total air and primary air supplied on the salt cake in the flue gas and smelt sulfidity were illustrated. The effects of primary air temperature and sulfur:sodium ratio on  $\text{SO}_2$  emission, smelt sulfidity, and total fume emission were also shown. Idealized models may be derived from the included graphical illustrations.

Clement, Coulter, and Suda (21) reported the current calculation procedure used by the Babcock & Wilcox Company to determine a material and heat balance for kraft recovery units. The effects of the liquor solids concentration and salt cake make-up on thermal efficiency is illustrated.

Thoen, DeHass, Tallent, and Davis (23) undertook a testing program to determine the concentration of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  upstream of the cascade evaporators under various operating conditions. It was reported that when the  $\text{SO}_2$ - $\text{H}_2\text{S}$  concentration was minimized, indicating sufficient oxygen and good turbulence, the steam production was maximized for a given liquor feed rate.

## Causticizing and Lime Recovery

In development of a causticizing and lime recovery expression Carroll (1) used a stoichiometric approach assuming constant 90% lime availability and 10% additional loss due to unconverted lime. He has also assumed that 4% (of total impure lime) make-up would be required. Carroll assumed a heat requirement of  $9 \times 10^6$  B.T.U. per ton O.D. lime produced for a constant 60% solids mud feed to the lime kiln.

Boyle and Tobias (2) neglected calculations of the variation in causticizing and lime recovery costs with respect to hydroxide requirements per ton of air-dried pulp in their kraft mill simulation equations.

Prakash and Murray (17) reported on the effects of process variables on  $H_2S$  emission during calcining. They conclude that sodium sulfide in the water soluble form is essentially the source of  $H_2S$  emission from lime kilns and results show that  $H_2S$  emission may be minimized by reducing the water content of the lime mud to the kiln. Oxidation seems to minimize the release of  $H_2S$  emission. Graphs were presented from which regression equations could be obtained.

## The Base Energy Balance

The object of a base energy balance is to compute gross high-pressure steam generated in the recovery boiler and determine the steam requirements for cooking, black liquor heating, and evaporation.

Carroll, in his work, considered a turbogenerator feed from recovery unit steam with extracted steam being used for the evaporators, black liquor heaters, and digesters.

Boyle and Tobias neglected the area of black liquor heating in calculation of steam requirements.

Both abovementioned works neglected the effect of continuous blow-down on the recovery unit.

### Optimization

Once a model equation is formulated in the form

$$E = f (X_1, X_2, X_3 \dots X_n)$$

restrictions about each of the variables ( $X_1, X_2, \dots X_n$ ) must be determined before an iterative procedure can be applied to the model.

Carroll defined some of the key restraints on his variables and developed the Created Response Surface Technique (CRST) for optimization of a nonlinear function subject to restraints.

The CRST is a steepest ascent technique in that it follows the steepest slope of the surface of the function up to the maximum, although, in its path up the surface it is imposed with increasingly stricter penalties as it approaches restraint boundaries.

To utilize the CRST in optimizing his mathematical model, Carroll wrote a Fortran computer program which left step size,  $h$ , and the restriction factor,  $r$ , for user input. By the choice of  $h$  and  $r$  Carroll was able to guide the optimization.

## DISCUSSION OF WORK

In an age of increasing use of computer technology to control and optimize processes, it seems desirable to program the optimization in a manner in which no user input is required. That is, in the case of the CRST, automatic step and restriction factor reduction is desirable. This would allow a computer to continually monitor process conditions and decide, perhaps many times a day, which values of each of the optimized process parameters would maximize profit.

The Model

The following model describes the economic performance of the unbleached kraft pulp mill described in Figure I as a function of process variables. The model uses as its basis a material balance based on one air-dried ton of pulp off the washer and a heat balance which refers to a datum of 80° F.

The framework of the model is that suggested by Boyle and Tobias (2). The wood and water relationships are taken directly from their work as are the major chemical relationships except as noted in the text. Production relationships were derived as noted with engineering balances derived by the author. The heat balance and economic relationships contain work done by Boyle and Tobias and expansions by the author as explained in the text.

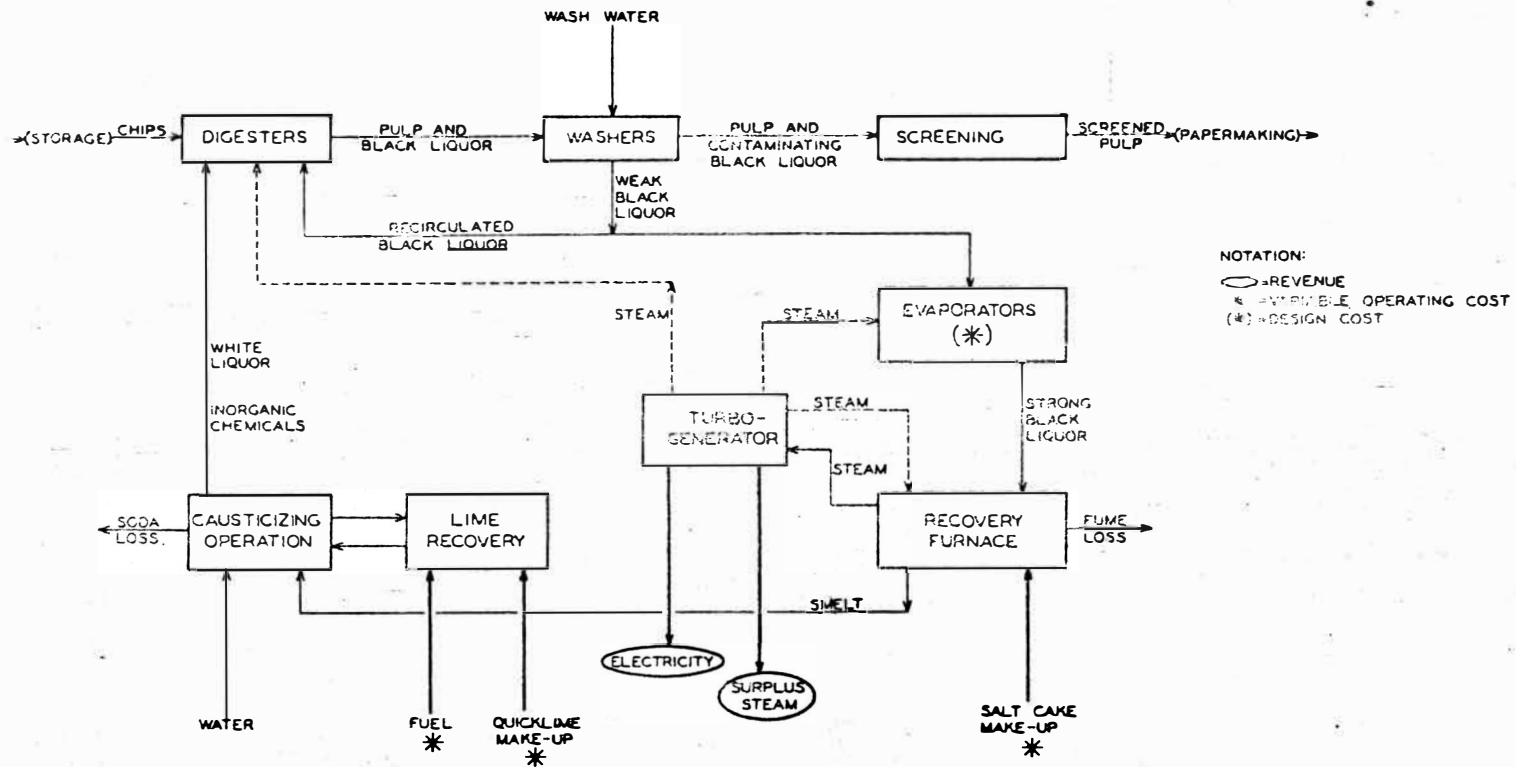


Figure I. Simplified Flow Diagram of Hypothetical Kraft Pulping System



Wood Relationships

$$1. \quad WS = 1800/Y$$

WS = solids in wood, lb/A.D.T. pulp

Y = yield fraction, nondimen

$$2. \quad WT = WS/(1-WM)$$

WT = total weight of wet wood, lb/A.D.T. pulp

WS = solids in wood, lb/A.D.T. pulp

WM = moisture in wood fraction, nondimen

$$3. \quad WW = WT - WS$$

WW = water in wood, lb/A.D.T. pulp

WT = total weight of wet wood, lb/A.D.T. pulp

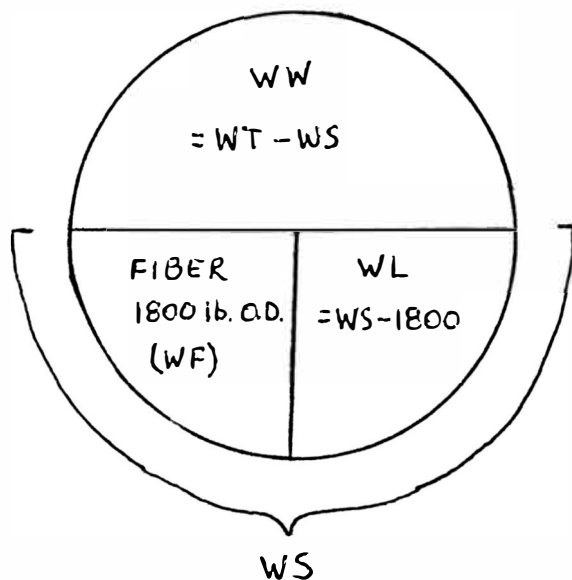
WS = solids in wood, lb/A.D.T. pulp

$$4. \quad WL = WS - 1800$$

WL = weight of removable lignin solids, lb/A.D.T. pulp

WS = solids in wood, lb/A.D.T. pulp

The derivation of the wood relationships is shown easily by the following diagram. The entire circle represents WT, or total wet wood charged to the digester per A.D.T. pulp.



Water Balance

$$5. \text{ VWL} = \text{WS}(\text{AA})/\text{AC}$$

VWL = Volume of white liquor,  $\text{ft.}^3/\text{A.D.T. pulp}$

WS = Solids in wood,  $\text{lb}/\text{A.D.T. pulp}$

AA = Active alkali,  $\text{lb}/\text{lb O.D. wood}$

AC = Active alkali concentration,  $\text{lb}/\text{ft.}^3$

$$6. \text{ VBL} = \text{VTL} - \text{VWL}$$

VBL = Volume of black liquor charged to digester,  $\text{ft.}^3/\text{A.D.T. pulp}$

VTL = Total volume of liquor in digester,  $\text{ft.}^3/\text{A.D.T. pulp}$

VWL = Volume of white liquor,  $\text{ft.}^3/\text{A.D.T. pulp}$

$$7. \text{ GP} = 1800 (1-\text{CW})/\text{CW}$$

GP = Liquor leaving system in pulp,  $\text{lb}/\text{A.D.T. pulp}$

CW = Consistency fraction of pulp off washer, nondimen

$$8. \text{ HCD} = (\text{CPS})(\text{WS}) + \text{WW} + 62.4 (\text{VTL})$$

HCD = heat capacity of digester contents,  $\text{BTU}/^\circ\text{F. per A.D.T. pulp}$

CPS = specific heat of wood solids,  $\text{BTU}/\text{lb } ^\circ\text{F.}$

WS = wood solids,  $\text{lb}/\text{A.D.T. pulp}$

WW = water in wet wood,  $\text{lb}/\text{A.D.T. pulp}$

VTL = total volume of liquor,  $\text{ft.}^3 \text{ A.D.T. pulp}$

$$9. \text{ GB} = \text{HCD} (\text{TT}-212)/\text{HLW}$$

GB = blow flow rate,  $\text{lb}/\text{A.D.T. pulp}$

HCD = heat capacity of digester contents,  $\text{BTU}/^\circ\text{F. per A.D.T. pulp}$

TT = top cooking temperature,  $^\circ\text{F.}$

HLW = latent heat of water at  $220^\circ \text{F.}$ ,  $\text{BTU}/\text{lb.}$

Note: Equation 8 neglects the heat capacity of the digester shell.

Water Balance (continued)

$$10. \quad GW = WW + 62.4 (VWL + VFW) - GB - GP$$

GW = water in liquor to evaporators, lb/A.D.T. pulp

WW = water in wood, lb/A.D.T. pulp

VWL = volume of white liquor to digester,  $\text{ft.}^3/\text{A.D.T. pulp}$

VFW = volume of fresh water to washer,  $\text{ft.}^3/\text{A.D.T. pulp}$

GB = vapor from blow tank, lb/A.D.T. pulp

GP = liquor leaving system in pulp, lb/A.D.T. pulp

$$11. \quad DF = 62.4 \text{ VFW}/2000$$

DF = dilution factor, lb.  $\text{H}_2\text{O}/\text{lb A.D. pulp}$

VFW = volume of fresh water to washer, lb/A.D.T. pulp

See Figure II for a diagrammatic description of the water balance.

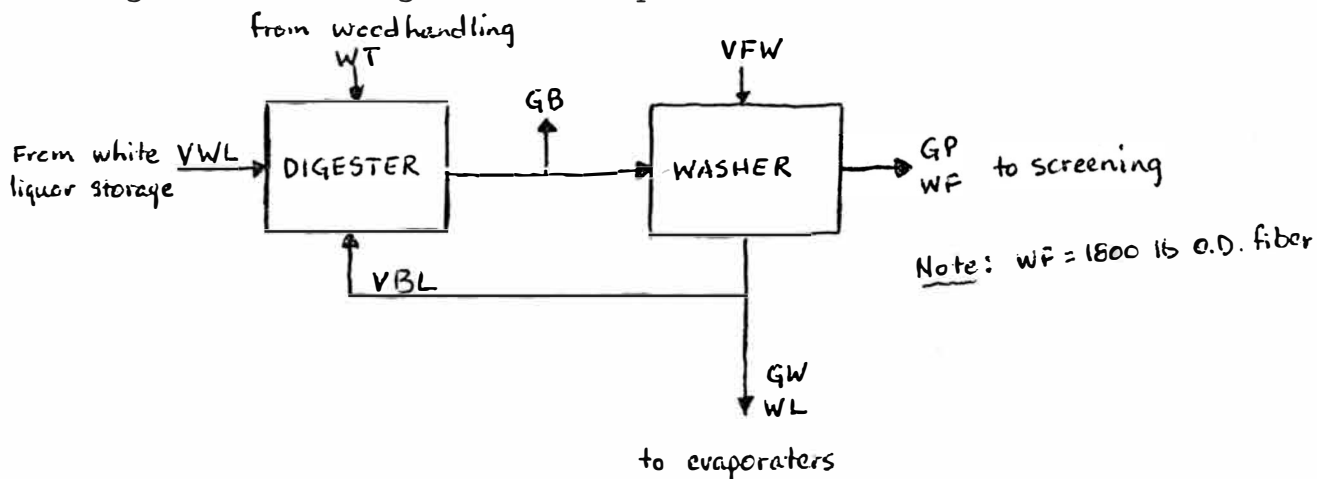


FIGURE II WATER BALANCE

Chemical Balance

$$12. \quad X1 = 1800 (1-S)AA/Y$$

X1 = weight of NaOH as Na<sub>2</sub>O, lb/A.D.T. pulp

S = sulfidity, %

AA = active alkali, lb/lb. O.D. wood

Y = yield, nondimen

$$13. \quad X2 = (S)X1/(1-S)$$

X2 = weight of Na<sub>2</sub>S as Na<sub>2</sub>O, lb/A.D.T. pulp

S = sulfidity, %

X1 = weight of NaOH as Na<sub>2</sub>O, lb/A.D.T. pulp

$$14. \quad X3 = (1-RD)X2/RD$$

X3 = weight of Na<sub>2</sub>SO<sub>4</sub> as Na<sub>2</sub>O, lb/A.D.T. pulp

RD = furnace reduction ratio, nondimen

X2 = weight of Na<sub>2</sub>S as Na<sub>2</sub>O, lb/A.D.T. pulp

$$15. \quad X4 = (1-EC) X1/EC$$

X4 = weight of Na<sub>2</sub>CO<sub>3</sub> as Na<sub>2</sub>O, lb/A.D.T. pulp

EC = causticizing efficiency, nondimen

X1 = weight of NaOH as Na<sub>2</sub>O, lb/A.D.T. pulp

$$16. \quad UL = 1.1 (.903 X4)$$

UL = lime usage, lb/A.D.T. pulp (assuming 10% in excess of that theoretically required)

X4 = weight of Na<sub>2</sub>CO<sub>3</sub> as Na<sub>2</sub>O, lb/A.D.T. pulp

$$17. \quad UML = .04 UL$$

UML = weight of make-up lime, lb/A.D.T. pulp (assuming 4% make-up required)

UL = usage of lime, lb/A.D.T. pulp

$$18. \quad SO2K = 820.6 \text{ NGP} + .45 \text{ NGF} + 9.09 \text{ KDRAFT}$$

SO2K = SO<sub>2</sub> loss at kiln, ppm

NGP = natural gas pressure, lb/in.<sup>2</sup>

NGF = natural gas flow, cfm

KDRAFT = kiln draft, in. H<sub>2</sub>O

$$19. \text{SO}_2\text{KL} = (\text{SO}_2\text{K})(\text{KAF})1440/\text{PR}(4.6 \times 10^{-8})$$

$\text{SO}_2\text{KL}$  =  $\text{SO}_2$  loss at kiln, lb S/A.D.T. pulp

$\text{SO}_2\text{K}$  =  $\text{SO}_2$  loss at kiln, ppm

$\text{KAF}$  = kiln air flow, CFM

$\text{PR}$  = production rate, A.D.T./day

$4.6 \times 10^{-8}$  = conversion factor to change  $\text{ft.}^3/\text{A.D.T.}$  to lb. S./A.D.T. pulp

(see note)

NOTE: The conversion factor was derived in the following manner:

560/492 converts CFM to STP

32/64 converts from lb.  $\text{SO}_2$  to lb. S

1/359 = lb. moles/ $\text{ft.}^3$

29 = lb. air/lb. - mole

$10^{-6}$  converts ppm parts

$$(560/492)(1/359)(29)(10^{-6})(32/64) = 4.6 \times 10^{-8}$$

$$20. \text{SO}_2\text{RB} = 2358 + .75 \text{ SP} - 2.55 \text{ FWF} + 6.88 \text{ PAF} + 2.7 \text{ SAF} + 22.37 \text{ TAF} \\ - 27.09 \text{ FSE} - 36.67 \text{ NOZP} - 32.02 \text{ NOZS} - 15.79 (2.29 \times 6) \\ + 24.06 \text{ GLALK} - 1.22 \text{ BEGT} + 2.82 \text{ CEGT} - 86.38 \text{ SAD} \\ - 35.84 \text{ TAD} + 727.51 \text{ FD} + 11.4 \text{ GLSULF}$$

$\text{SO}_2\text{RB}$  =  $\text{SO}_2$  loss at recovery boiler, ppm

$\text{SP}$  = steam pressure, psig

$\text{FWF}$  = feedwater flow, lb/hr.

$\text{PAF}$  = primary air flow, CFM

$\text{SAF}$  = secondary air flow, CFM

$\text{TAF}$  = tertiary air flow, CFM

$\text{FSE}$  = solids fraction of feed liquor, to furnace, nondimen

$\text{NOZP}$  = nozzle pressure of black liquor sprayer, psig

$\text{NOZS}$  = nozzle size of black liquor sprayer, inches

$\text{X6}$  = weight of salt cake make-up as  $\text{Na}_2\text{O}$ , lb/A.D.T. pulp

$\text{GLALK}$  = green liquor alkalinity

$\text{BEGT}$  = boiler exit gas temperature, °F.

$\text{CEGT}$  = cascade exit gas temperature, °F.

$\text{SAD}$  = secondary air draft, in.  $\text{H}_2\text{O}$

$\text{TAD}$  = tertiary air draft, in.  $\text{H}_2\text{O}$

$\text{FD}$  = total furnace draft, in.  $\text{H}_2\text{O}$

$\text{GLSULF}$  = green liquor sulfidity, nondimen

$$21. \text{TOAF} = \text{PAF} + \text{SAF} + \text{TAF}$$

$\text{TOAF}$  = total air flow, CFM

$\text{PAF}$  = primary air flow, CFM

$\text{SAF}$  = secondary air flow, CFM

$\text{TAF}$  = tertiary air flow, CFM

$$22. \text{SO}_2\text{RBL} + (\text{SO}_2\text{RB})(\text{TOAF})(1440/\text{PR})(4.6 \times 10^{-8})$$

$\text{SO}_2\text{RBL}$  =  $\text{SO}_2$  loss at furnace, lb. S/A.D.T. pulp

$\text{SO}_2\text{RB}$  =  $\text{SO}_2$  loss at furnace, ppm

$\text{PR}$  = production rate, A.D.T./day

The conversion factor  $4.6 \times 10^{-8}$  was determined for the lime kiln and is used again here.

Equations 18 and 20 were the result of work done by SHouou-I Wang, Montana State University, as a Doctoral Dissertation.

$$23. \text{X5} = \text{SO}_2\text{KL} + \text{SO}_2\text{RBL}$$

$\text{X5}$  = make-up sulfur required, lb/A.D.T. pulp

$\text{SO}_2\text{KL}$  =  $\text{SO}_2$  loss at kiln, lb. S/A.D.T. pulp

$\text{SO}_2\text{RBL}$  =  $\text{SO}_2$  loss at furnace, lb. S/A.D.T. pulp

$$24. \text{X6} = 12.5/(\text{D.F.} + .085) + 12$$

$\text{X6}$  = make-up salt cake as  $\text{Na}_2\text{O}$ , lb/A.D.T.

$\text{DF}$  = dilution factor, lb.  $\text{H}_2\text{O}$ /lb. A.D. pulp

Equation 24 was taken from Carroll's dilution factor curve (see figure 3)

Chemical balance equations 12 through 15 were derived from the following:

$$\text{X1} + \text{XZ} = 1800 \text{ AA/Y} \quad \text{Definition of active alkali}$$

$$\text{S} = \text{X2}/(\text{X1} - \text{X2}) \quad \text{Definition of sulfidity}$$

$$\text{Furnace reduction ratio} = \frac{\text{X}_2}{\text{X}_2 + \text{X}_3} = \text{RD}$$

$$\text{Causticizing efficiency} = \text{EC} = \frac{\text{X}_1}{\text{X}_1 + \text{X}_4}$$

#### Cooking and Production

$$(43.20 - 16113/\text{TT} + 273)$$

$$25. \text{H} = (\text{ZUT}/300 + \text{ZC}/60)(2.718)$$

$\text{H}$  = H factor

$\text{ZUT}$  = time up to temperature, min.

$\text{ZC}$  = cook time, min.

$\text{TT}$  = top temperature of cook, °F.

The basis for this equation is that of Arrhenius,

$$\ln r = B - A/T$$

where R = relative reaction rate

T = temperature in °K

and B and A are constants,

$$B = 43.20 \text{ and } A = 16,113$$

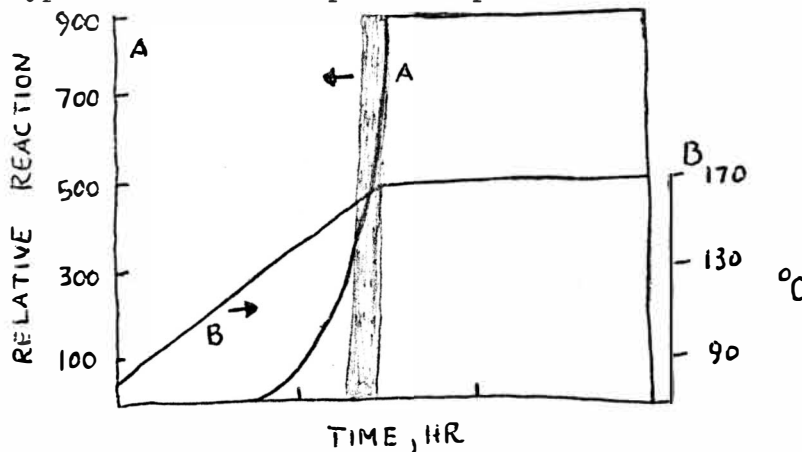
$$X = e^{\ln x} \text{ implies } R = e^{B - \frac{A}{T}}$$

Vroom defined H factor as  $H = Rt$  where  $t$  = time in hours

It follows that,

$$H = t_c e^{(43.20 - \frac{16113}{T})} \text{ where } T = \text{abs. temperature} \text{ and } t_c = \text{time of cook, hrs.}$$

Looking at a typical time vs. temperature plot



It is apparent that either an approximation of the average time up to temperature or an approximation of the average temperature during heat-up is needed to calculate H. It was assumed that

$$\int_0^{t@tt} T dt = \left(\frac{1}{5} \text{ time up to temp.}\right)(\text{top temperature})$$

(note the area under the heat-up part of curve A as compared to the shaded area,  $A^1$ ).

Finally, if the time up to temperature, ZUT, is in minutes as is the time of the cook at top temperature, ZC, and the top temperature,

$$H, \text{ is in } ^\circ\text{F.}, \quad H = \left(\frac{ZUT}{5 \times 60} + \frac{ZC}{60}\right)(2.718 \left(43.20 - \frac{16113}{TT-273}\right))$$

$$26. P = (5711 \text{ RLW} \cdot 2144) / (\text{AA} \cdot 913 \text{ H} \cdot 399)$$

$$27. Y = 19.43 + .73P$$

P = permanganate no.

RLW = liquor to wood ratio, lb. liquor/lb. wood

AA = active alkali, lb/lb. O.D. wood

H = H factor

Y = yield, %

The above two equations were derived using a regression analysis of mill data. These particular equations are in use for dedicated computer digester control by Owens-Illinois at their Valdosta mill.

$$28. \text{AE} = (\text{X1} + .5 \text{ X } 2) / \text{WS}$$

AE = effective alkali, lb/lb. O.D. wood

X1 = weight of NaOH as Na<sub>2</sub>O, lb/A.D.T. pulp

X2 = weight of Na<sub>2</sub>S as Na<sub>2</sub>O, lb/A.D.T. pulp

WS = solids in wood, lb/A.D.T. pulp

$$29. \text{RLW} = (62.4 (\text{VWL} + \text{VBL}) + \text{WW}) / \text{WS}$$

RLW = liquor:wood ratio, lb/lb O.D. wood

VWL = volume of white liquor to digester, ft.<sup>3</sup> A.D.T. pulp

VBL = volume of black liquor to digester, ft.<sup>3</sup> A.D.T. pulp

WW = water in wood, lb/A.D.T. pulp

WS = solids in wood, lb/A.D.T. pulp

$$30. \text{PR} = 1440 (\text{QN})(\text{C}) / (\text{ZF} + \text{ZUT} - \text{ZC})$$

PR = production rate, A.D.T./day

ZC = time at top temperature, min./batch

ZF = time to fill digester, min./batch

ZUT = time up to temperature, min./batch

C = capacity of 1 digester, A.D.T./batch

QN = number of digesters, nondimen

$$31. \text{SW} = \text{WL} + 1.29 \text{ X1} + 1.26 \text{ X2} + 2.29 \text{ X3} - 1.71 \text{ X4}$$

SW = solids in liquor to evaporators, lb/A.D.T.

WL = weight of removable "lignin" solids, lb/A.D.T.

X1 = caustic as Na<sub>2</sub>O in cook, lb/A.D.T.

X2 = Na<sub>2</sub>S as Na<sub>2</sub>O in cook, lb/A.D.T.

X3 = Na<sub>3</sub>SO<sub>4</sub> as Na<sub>2</sub>O in cook, lb/A.D.T.

X4 = Na<sub>2</sub>CO<sub>3</sub> as Na<sub>2</sub>O in cook, lb/A.D.T.



$$32. \text{ FSW} = \text{SW}/(\text{SW} + \text{GW})$$

FSW = solids fraction in liquor to evaps. nondimen  
 SW = solids in wood, lb/A.D.T. pulp  
 GW = water in liquor to evaporators, lb/A.D.T.

$$33. \text{ GE} = \text{SW}(1-\text{FSE})/\text{FSE}$$

GE = water in liquor to furnace  
 SW = solids in wood, lb/A.D.T. pulp  
 FSE = solids fraction in liquor to furnace, nondimen

$$34. \text{ GEV} = \text{GW} - \text{GE}$$

GEV = evaporation rate from evaporators, lb/A.D.T.  
 GW = water in liquor to evaporators, lb/A.D.T. pulp  
 GE = water in liquor to furnace, lb/A.D.T. pulp

$$35. \text{ SS} = \text{SW} - \text{WL}$$

SS = smelt solids, lb/A.D.T.  
 SW = solids in liquor to evaporators, lb/A.D.T.  
 WL = removable "lignin" solids, lb/A.D.T.

$$36. \text{ GLHV} = 6600 \text{ SW}$$

GLHV = gross liquor heating value, BTU/A.D.T.  
 SW = solids in wood, lb/A.D.T. pulp

NOTE: The value 6600 BTU/lb. B.L. solids was taken from Pulp and Paper  
 Manufacture, Vol. 1, p. 622.

$$37. \text{ EBL} = (\text{SW})(\text{CP})(\text{FLT}-80)/\text{FSE}$$

EBL = enthalpy of black liquor to furnace, BTU/A.D.T. pulp  
 SW = black liquor solids, lb/A.D.T. pulp  
 CP = heat capacity of black liquor, BTU/lb. °F.  
 FLT = feed liquor temperature, °F.  
 FSE = solids fraction in liquor to furnace, nondimen

$$38. \text{ EHA} = (1440 \text{ TOAF}/\text{PR})(1/1.013)(.24)(\text{CEGT}-80)(29)(540/492)(1/359)$$

EHA = the enthalpy of enthalpy of air supplied to recovery unit,  
 BTU/A.D.T. pulp  
 TOAF = total air flow, CFM  
 PR = production rate, A.D.T./day  
 CEGT = cascade exit gas temperature, °F.

The enthalpy of air supplied to the recovery unit is calculated assuming a heat capacity for air of .24 BTU/lb. °F. and that the air is 80° F. and 60% R.H. (Humidity = .013 lb. H<sub>2</sub>O/lb. dry air).

$$39. \quad CER = \frac{SW(1-FSE)}{FSE} - \frac{SW(1-FSC)}{FSC}$$

CER = cascade evaporation rate, lb/A.D.T. pulp  
 SW = black liquor solids, lb. A.D.T. pulp  
 FSE = solids fraction in liquor to cascades, nondimen  
 FSC = solids fraction in liquor to furnace, nondimen

$$40. \quad EAW = (1440 \text{ TOAF/PR})(.013/1.013)(29)(540/492)(1/359)$$

EAW = enthalpy of water in air supplied to furnace, lb/A.D.T. pulp  
 TOAF = total air flow, CFM  
 PR = production rate, A.D.T./day

The enthalpy of water in air supplied to the recovery unit is calculated assuming a heat capacity of water of 1 BTU/lb. °F. The enthalpy of infiltrated air is ignored.

$$41. \quad DGL = (1440 \text{ TOAF/OR})(560/492)(1/359)(29)(1/1.013) + (1.56SW)(24)(CEGT-80)$$

DGL = dry gas heat loss from recovery unit, BTU/A.D.T. pulp  
 TOAF = total air flow, CFM  
 PR = production rate, A.D.T./day  
 SW = black liquor solids, lb/A.D.T. pulp  
 CEGT = cascade exit gas temperature °F.

The dry gas heat loss is calculated assuming a heat capacity for the flue gas of .24 BTU/lb. °F. The term 1.56 SW accounts for the CO<sub>2</sub> generated during combustion and is estimated from the following black liquor analysis:

Elemental Black Liquor Analysis

Carbon	42.6
Hydrogen	3.8
Sulfur	2.7
Sodium	19.1
Inert oxides	.2
Oxygen	<u>31.6</u>
	100.0 lb.

$$\text{CO}_2 \text{ formed} = (42.6/100)(44/12) = 1.56 \text{ lb. CO}_2/\text{lb. B.L. solids}$$

$$42. \text{ WVF} = \frac{\text{SW}(1-\text{FSE})}{\text{FSE}} + .342 \text{ SW} + \left(\frac{1440 \text{ TOAF/PR}}{540/492}\right)\left(\frac{.013}{1.013}\right)(29)$$

WVF = water vapor loss to flue, lb/A.D.T. pulp

SW = black liquor solids, lb/A.D.T. pulp

FSE = solids fraction in liquor to cascades, nondimen

TOAF = total air flow, CFM

The term  $\text{SW}(1-\text{FSE})/\text{FSE}$  accounts for the water entering with the liquor. The term  $.342\text{SW}$  accounts for water formed from hydrogen during combustion (also estimated from the above B.L. analysis). The last term accounts for humidity of the entering air.

$$43. \text{WVL} = \text{WVF} (1192 - 80 + 32)$$

WVL = heat loss due to water in furnace flue, BTU/A.D.T. pulp

WVF = water vapor loss to flue, lb/A.D.T. pulp

The water vapor heat loss is calculated assuming that the flue gas exists at 300° F. and 1 atm. pressure ( $\lambda = 1192$ ).

$$44. \text{ESMEL} = (.411 \text{ SW} + 2.29 \times 6) 532$$

ESMEL = enthalpy of smelt from the recovery unit, BTU/A.D.T. pulp

SW = black liquor solids, lb/A.D.T. pulp

X6 = weight of make-up salt cake as  $\text{Na}_2\text{O}$ , lb/A.D.T. pulp

The enthalpy of smelt from the recovery unit is calculated assuming that it takes 532 BTU/lb. to melt smelt and raise it to a temperature of 1550° F. The term  $.411 \text{ SW}$  accounts for the weight of smelt formed, lb/A.D.T. pulp, and is calculated from the previous black liquor analysis and the following smelt analysis as shown:

Smelt Analysis

$\text{Na}_2\text{S}$	25.55%	as Na
$\text{Na}_2\text{SO}_4$	.25%	as Na
$\text{Na}_2\text{CO}_3$	74.21%	as Na
	100.00%	

From the previous elemental black liquor analysis, it is known that

$$\begin{array}{rcl}
 \text{lb. Na} & = & 19.1 \text{ lb}/100 \text{ lb. BL solids} = .191 \text{ lb}/\text{lb. BL solids} \\
 \text{so lb. Na}_2\text{S} & = & (.191 \text{ SW})(.2555)(78/46) = .0827 \text{ SW} \\
 \text{lb. Na}_2\text{SO}_4 & = & (.191 \text{ SW})(.0024)(142/46) = .0014 \text{ SW} \\
 \text{lb. Na}_2\text{CO}_3 & = & (.191 \text{ SW})(.7421)(106/46) = \underline{.3266 \text{ SW}} \\
 & & \underline{.411 \text{ SW}}
 \end{array}$$

Thus, smelt formed = .411 SW

$$45. \text{ REDL} = (2.29X6)RD(3000)$$

REDL = loss of heat in reducing make-up salt cake, BTU/A.D.T. pulp  
 X6 = weight of make-up salt cake as  $\text{Na}_2\text{O}$ , lb/A.D.T. pulp  
 RD = furnace reduction ratio, nondimen

The heat required for the reduction of salt cake may be calculated from the standard heats of formation of  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{SO}_4$ . This value is 3000 BTU/lb.  $\text{Na}_2\text{SO}_4$ .

$$46. \text{ HRC} = 428 \text{ SW}$$

HRC = heat of reaction correction, BTU/A.D.T. pulp  
 SW = black liquor solids, lb/A.D.T. pulp

The heat of reaction correction term must be calculated to account for the fact that the gross liquor heating value calculation was based on findings of bomb calorimeter studies. The heat of reaction correction term compensates for the difference in furnace and bomb calorimeter combustion products. The value of 428 BTU/lb. B.L. solids was taken from Pulp and Paper Manufacture, Vol. 1, Chapter 10.

$$47. \quad HP = GLHV + EBL + EHA + EAW + DGL - WV - ESME - REDL - HRC - HCD - (TT - 80) - (HLW) / (GEV / EEV)$$

HP = net heat produced by recovery boiler for process steam BTU/A.D.T. pulp

GLHV = gross liquor heating value, BTU/A.D.T. pulp

EBL = enthalpy of black liquor to furnace, BTU/A.D.T. pulp

EHA = enthalpy of heated air supplied, BTU/A.D.T. pulp

EAW = enthalpy of water in air supplied, BTU/A.D.T. pulp

DGL = dry gas heat loss, BTU/A.D.T. pulp

WV = water vapor heat loss, BTU/A.D.T. pulp

ESME = enthalpy of smelt, BTU/A.D.T.

HRC = heat of reaction correction, BTU/A.D.T.

HCD = heat capacity of digester contents, BTU/A.D.T. pulp

TT = top cooking temperature, °F.

HLW = latent heat of water, BTU/lb.

GEV = evaporation rate from evaporators, lb/A.D.T.

EEV = evaporator economy, nondimen

The net heat available for steam production is calculated by difference of heat inputs and heat outputs from the recovery unit. Input of heat due to direct steam liquor heating as well as the heat loss due to fume up the flue are ignored. Note that the term  $(HCD)(TT-80)$  accounts for steam to heat the digester during cooking ignoring radiation loss. The term  $(HLW) (GEV/EEV)$  accounts for steam supplied to the multiple effect evaporators. Note that EEV, evaporator economy, will change as steam usage and production rate vary. This implies that a good average approximation of EEV should be used and adjusted for ranges far from the average.

$$48. \quad UF = (FCFM)(HOCF)(144)/1000PR$$

UF = usage of kiln fuel, MBTU/A.D.T.

FCFM = lime kiln fuel consumption, CFM/A.D.T.

HOCF = heat of combustion of natural gas, BTU/ft.<sup>3</sup>(-1065)

PR = production rate, A.D.T./day

$$49. \quad CC = (P1)(1.71X5) + (P2)(2.29X6) + P3UML + PAUF$$

CC = chemicals cost, \$/A.D.T.  
 PI = price of sulfur, \$/lb.  
 X5 = weight of make-up sulfur, lb/A.D.T.  
 P2 = price of salt cake, \$/lb.  
 X6 = weight of make-up salt cake, lb/A.D.T.  
 P3 = price of lime, \$/lb.  
 UML = weight of make-up lime, lb/A.D.T.  
 P4 = price of natural gas, \$/MBHL

$$50. \quad CNP = CC - (PS)(.001 \text{ HP})$$

CNP = recovery system net cost, \$/A.D.T.  
 CC = chemicals cost, \$/A.D.T.  
 PS = value of process heat, \$/MBTU  
 HP = heat produced in recovery process, BTU/A.D.T.

$$51. \quad RT = V - CNP - CWV - F/PR$$

RT = return on pulp, \$/A.D.T.  
 V = value of slush unbleached pulp, \$/A.D.T.  
 CNP = recovery system net cost, \$/A.D.T.  
 CWV = cost of wood, \$/A.D.T. pulp  
 F = fixed (nonvariable) costs of pulp process, \$/day  
 PR = production rate, A.D.T./day

$$52. \quad R = (PR)(RT)$$

R = total return on process  
 PR = production rate, A.D.T./day  
 RT = return on pulp, \$/A.D.T.

CRST Investigation

To investigate the feasibility of automatic step size and restriction factor reduction, the following three-dimensional model was chosen:

$$E = 25 - (X-5)^2 - (Y-5)^2$$

subject to the following restrictions:

$$Y = .8X$$

$$Y = 8 - .8X$$

It should be mentioned that many three-dimensional model equations could have been chosen. This particular equation was chosen by Carroll (1) to check his optimization program and was useful for comparison of this work.

Figure III is a physical interpretation of the model and restrictions.

Figure IV is a statement of program logic used for CRST optimization utilizing automatic step-size and restriction factor reduction.

Appendix I lists the program statements corresponding to the Figure IV logic diagram. The model is included as a subroutine model and its restrictive equations are included as subroutine SUBA.

The program generates data on disk which is shown in Appendix II.

The main program and subroutine occupies approximately 6K of core and the output data approximately 4K on disk.

To initiate optimization it is necessary to input initial values of  $h$ ,  $r$ ,  $x$ , and  $y$ .

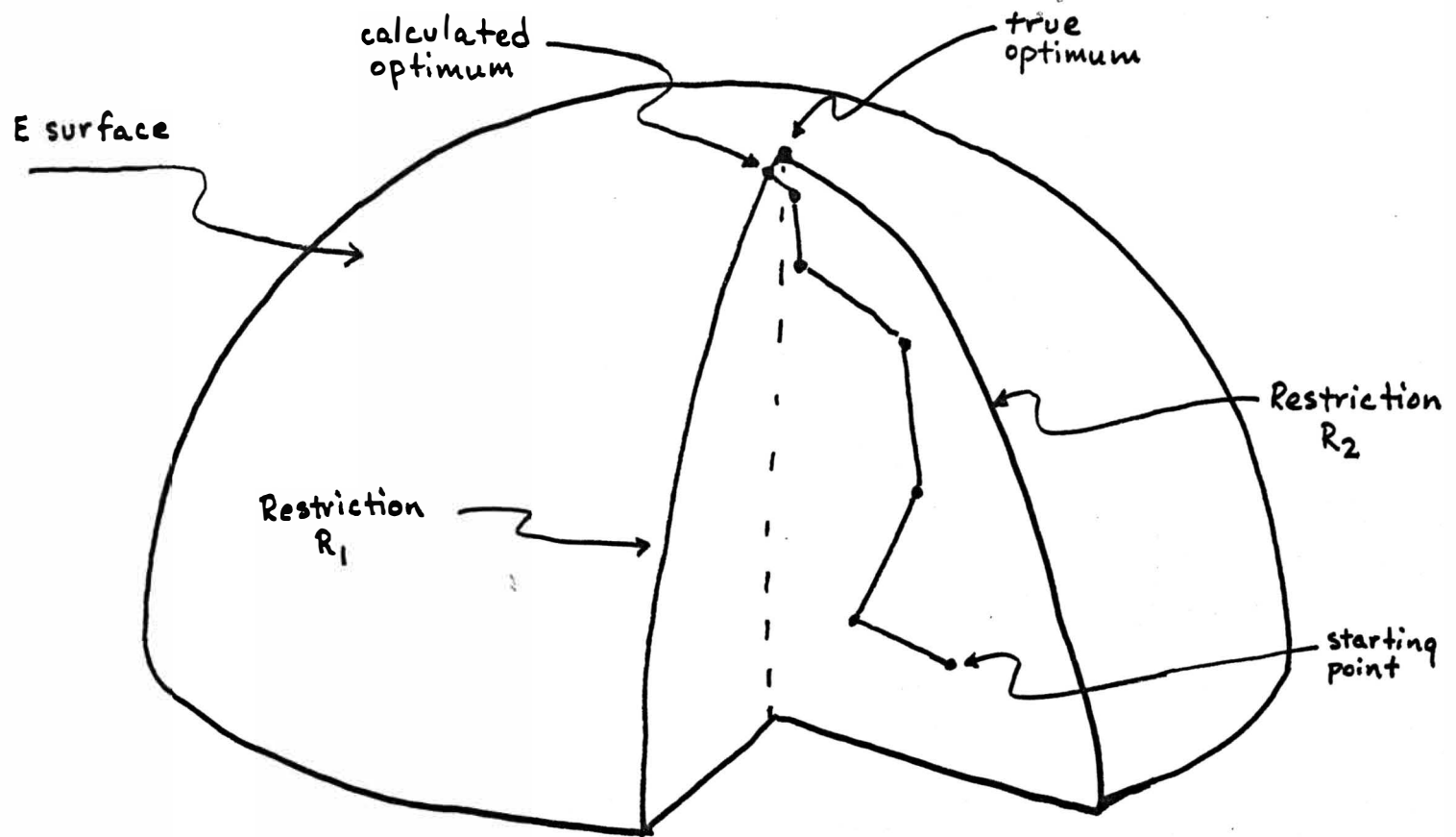
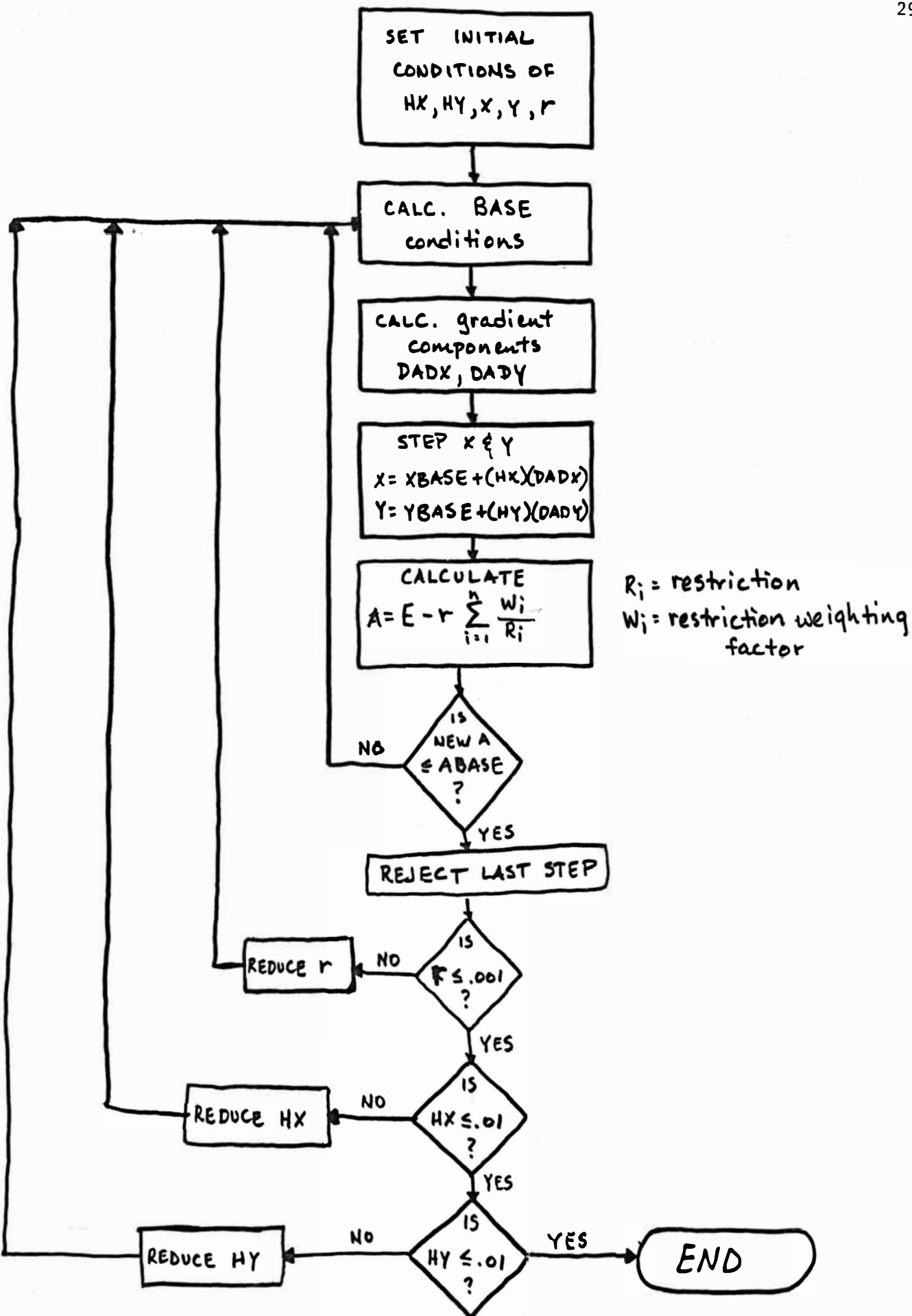


Figure III. Physical Interpretation of Model  $E = \sqrt{25 - (x-5)^2 - (y-5)^2}$   
w/ Restrictions R<sub>1</sub> and R<sub>2</sub>



Figure IV



### Construction of Restrictive Equations

In developing his restrictive equations, Carroll believed that it was only necessary to rearrange them to the form greater than or equal to zero.

It was found in developing the program of this thesis that trial and error manipulation of the form of the restrictive equations was necessary to insure that progress was in the correct direction and that convergence proceeded at an acceptable rate.

### Automatic Step Size Reduction Technique

The logic of the step size reduction technique employed is illustrated in Figure IV. The technique was derived by the author and features independent reductions of step size in the X and Y directions by comparison of progress of the current step toward the optimum with that of the previous step.

## RESULTS

The results of optimization using the CRST were as follows:

	<u>Actual</u>	<u>Calculated</u>	<u>% Error</u>	<u>Carroll's % Error</u> <sup>1</sup>
X	5.04	5.035	.16	.25
Y	3.88	3.877	.10	.20
Z	4.89	4.869	.09	

It can be seen in Appendix II that as the program approaches the optimum the progress becomes slower and slower (i.e. this method is quick to reach the area of the optimum but absolute convergence is slow).

## CONCLUSIONS

It is concluded that:

1. Automatic step size and restrictive factor reduction is feasible.
2. Restrictive equation construction must be a trial and error process for best results.
3. It may be desirable to utilize the CRST to get close to the optimum and then utilize another iterative technique (38, 39, 40) for absolute convergence.

## DISCUSSION OF INDUSTRIAL APPLICABILITY

It must be recognized that development of a mathematical model for a Kraft mill must be highly individualized for each mill. Each particular mill operates under its own peculiar conditions which must be accounted for.

The idealistic goal for utilization of the optimization using techniques investigated should incorporate hierarchal control. That is, several dedicated control computers throughout the process, each subserviant to the same central master computer.

The scope of such a control scheme is tremendous and the capital outlay significant. It is necessary, therefore, that such an arrangement be carefully considered and conservatively developed. Economic conditions at present make such a goal desirable only to the most far-sighted and capital rich corporations.

At the present time, the most desirable application is much like that of Boyle and Tobias (2) in which control is neglected and the model is used to direct managers as to their most profitable posture. Utilization in this manner allows many of the seemingly intangible factors of operation to be described tangibly.

APPENDIX I

```

DIMENSION AA(150), EE(150),
1 RR(150), DADX(150),
2 DADY(150), AB(150), XB(150), YB(150),
3 RSLM(150)
COMMON X,Y,A,E,R,WRES1,WRES2,RES1,RES2
IX=2
IY=2
PH=0
WRITE (21,5)
5 FORMAT (1H ,8HSTEP NO.,5H          ,2HXX,8H          ,2HHY,
1 8H          ,1HR,9H          ,1HX,9H          ,1HY,
2 8H          ,4HDADX,6H          ,4HDADY,6H          ,4HRES1,
3 8H          ,4HRES2,7H          ,1HF,9H          ,1HA)
READ (30,4) WRES1,WRES2
4 FORMAT (2F)
READ (30,4) XBASE,YBASE
READ (5,18) R,EX,HY
18 FORMAT (3F)
Y=YBASE
V=YBASE
CALL SUBA
ABASE=A
WRITE (5,6) ABASE,E,RES1,RES2,A
6 FORMAT (5(1X,F9.3))
11 DO 140 L=1,150
RR(L)=R
AB(L)=ABASE
XB(L)=XBASE
YB(L)=YBASE
X=XBASE+.1
Y=YBASE
CALL SUBA
AX=A
X=XBASE
Y=YBASE+.1
CALL SUBA
AY=A
DADX(L)=(AX-AB(L))/.1
IF (L-1) 9999,1,10
9 IF (DADX(L)*DADX(L-1)) 8,1,1
YBASE=YB(L-1)
YBASE=YB(L-1)
CALL SUBA
ABASE=A
HX=HY/2.
IX=IX+1
IF (IX-6) 17,17,110
7 GO TO 2
DADY(L)=(AY-AB(L))/.1
IF (L-1) 9999,3,20
2 IF (DADY(L)*DADY(L-1)) 9,3,3
XBASE=XB(L-1)
YBASE=YB(L-1)
CALL SUBA
ABASE=A
HY=HY/2.
IY=IY+1
IF (IY-6) 15,16,110
4 GO TO 2
X=XBASE+HX*DADX(L)

```



```

Y=YBASE+HY*DADY(L)
CALL SUBA
AA(L)=A
EE(L)=E
WRITE (21,7) L,HX,HY,RR(L),X9(L),YB(L),DADX(L),DADY(L),
1 RES1,RES2,EE(L),AA(L)
FORMAT (4X,I2,4X,11(F9.3,1X)/)
IF (ABASE-AA(L)) 50,60,60
ABASE=AA(L)
XBASE=X
YBASE=Y
40 CONTINUE
WRITE (5,1233)
233 FORMAT (1X,'L-ERR'/)
CALL EXIT
ABASE=AB(L)
XBASE=XB(L)
YBASE=YB(L)
IF (R-.001) 80,70,70
80 R=RR(L)/10.
X=XBASE
Y=YBASE
CALL SUBA
ABASE=A
GO TO 140
IF (HX-.01) 12,12,85
12 HX=0.
GO TO 13
15 HX=HX+.9
IF (HY-.01) 14,14,15
14 HY=0.
IF (RH=1) 140,40,9999
15 HY=HY+.9
GO TO 140
9999 WRITE (5,12345)
2345 FORMAT (1X,19999-ERR'/)
CALL EXIT
13 WRITE (5,321)
321 FORMAT (1X,'I-ERR'/)
CALL EXIT
40 WRITE (5,150)
50 FORMAT (1X,'OPTIMUM HAS BEEN REACHED'/)
END

```



SUBROUTINE SUBA

COMMON X,Y,A,E,R,WRES1,WRES2,RES1,RES2

37

E=(25.-(Y-E.)\*\*2-(Y-E.)\*\*2)\*\*\*.5

RES1=(Z,B)\*X-Y

RES2=B.-(C,B)\*X-Y

SUM=WRES1/RES1+WRES2/RES2

RSUM=R\*SUM

A=E-RSUM

RETURN

END

APPENDIX II

91	0.027	0.214	0.000	5.035	3.877	-0.286	0.220	0.144	0.101	4.872
92	0.025	0.212	0.000	5.035	3.877	-0.286	0.000	0.145	0.100	4.872
93	0.022	0.211	0.000	5.035	3.877	-0.286	0.000	0.145	0.100	4.872
94	0.022	0.210	0.000	5.035	3.877	-0.286	0.000	0.146	0.099	4.872
95	0.018	0.200	0.000	5.035	3.877	-0.286	0.000	0.146	0.099	4.872
96	0.016	0.000	0.000	5.035	3.877	-0.286	0.000	0.147	0.099	4.872
97	0.015	0.000	0.000	5.035	3.877	-0.286	0.000	0.147	0.098	4.872
98	0.013	0.000	0.000	5.035	3.877	-0.286	0.000	0.147	0.098	4.872
99	0.012	0.000	0.000	5.035	3.877	-0.286	0.000	0.148	0.098	4.872
00	0.011	0.000	0.000	5.035	3.877	-0.286	0.000	0.148	0.097	4.872
01	0.010	0.000	0.000	5.035	3.877	-0.286	0.000	0.148	0.097	4.872

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