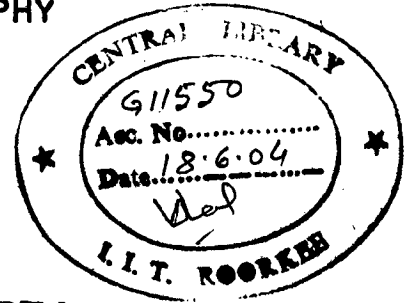


MATHEMATICAL MODELLING AND ANALYSIS OF PULP WASHING PROBLEM FOR OPTIMUM OPERATION

A THESIS

*Submitted in fulfilment of the
requirements for the award of the degree
of
DOCTOR OF PHILOSOPHY*



By

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DECEMBER, 2001

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in this thesis entitled, **"MATHEMATICAL MODELLING AND ANALYSIS OF PULP WASHING PROBLEM FOR OPTIMUM OPERATION"**, in fulfillment of the requirement for the award of the Degree of **Doctor of Philosophy** and submitted in the Department of Institute of Paper Technology of the Institute is an authentic record of my own work carried out during the period from January 1998 to November, 2001, under the supervision of Dr. A. K. Ray and Dr. V. P. Singh.

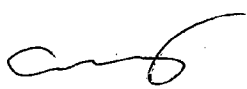
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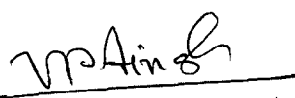
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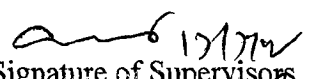
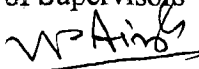

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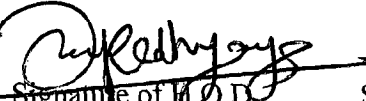
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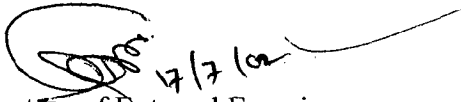

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Dated: December 28, 2001


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ABSTRACT

Mathematical modeling is an indispensable tool now a day to analyze, correlate, simulate, optimize and finally control of any chemical process plant. Pulp and paper industry –a core sector industry is not the exception. In fact, this industry is very capital intensive industry. Huge amount of raw materials, chemicals, energy, and water are consumed in the process of paper manufacture with requirement of large labor force generating an enormous quantum of pollution loads. Mathematical approach to quantify the optimal parameters will be of immense potential to alleviate this today's burning problem of paper industry's survival.

For sustainability in production of paper, it is imperative necessity to look in to all subsystems for their optimization and to explore the possibilities of eliminating the operational bottlenecks to fetch maximum economy.

In the present investigation both steady state mathematical and statistical modeling to the various interactive subsystems are attempted for optimizing a multi-stage brown stock washing (BSW) plant. Accordingly an objective function has been formulated based on minimum annual cost. This objective function involves terms related to other important operations such as multiple effect evaporator, multi-stage bleaching, effluent treatment plant along with usage of heating value of black liquor in recovery furnace operation. The minimum cost function comprises of costs due to washing equipments (P_w), maintenance and repair (P_M), power consumption for drum rotation back shower pump, vacuum pump, ($P_o * C_{13}$), for repulper-shredder ($P_o * C_5$), liquor spray ($P_o * C_6$) for screw conveyer at the last BSW ($P_o * C_4$), due to evaporation ($P_E * C_E$), steam for hot wash water ($P_A * C_A$), steam generated due to heat value of BLS ($P_E * C_L$), condensate saving ($P_s * C_s$), bleach chemical consumption due to carry over solids ($P_{NB} * C_{NB}$), and labor cost (C_{LW}), cost of effluent

treatment($P_{\text{Eff}}*C_{\text{Eff}}$), cost due to soda loss($P_{\text{Sl}}*C_{\text{Sl}}$), cost due to solid loss($P_{\text{tsl}}*C_{\text{tsl}}$). The objective function is modeled as follows:

$$\text{Min } (C_T) = (P_w + P_m) * N + P_E * (C_E + C_A + C_L) + P_s * C_S + P_{NB} * C_{NB} + (C_{13} * N + C_5 * (N-1) + C_6 * N + C_4) * P_o + C_{LW} + P_{\text{Eff}} * C_{\text{Eff}} + P_{\text{Sl}} * C_{\text{Sl}} + P_{\text{tsl}} * C_{\text{tsl}}$$

Where C_{13} = power consumption due to drum rotation (C_1) + back shower pump (C_2) + vacuum pump (C_3). For solution of the above objective function, the decision variables are dilution factor (DF) and number of stages (N). For optimization and simulation purpose each terms require model development as a function of DF and N in various subsystem of a paper mill. The interactive subsystems as envisaged in the objective function are BSW, MEE, multi-stage bleach plant, effluent treatment plant (ETP) and recovery furnace operation for steam generation. Each in turn demands development of mathematical models. In order to develop models in all the subsystems, a typical Indian mill configuration using hardwood / bamboo with normal operational conditions has to be known.

For BSW operation static models for fluid flow through porous medium (mat in this case) has been employed to estimate different operational and design parameters. Equations are also developed for power consumption calculations. Where equations are not available, data has been collected from a running Kraft mill using hardwood and bamboo. For simulation purpose, worst conditions are considered.

Various algorithms have been constructed for solid reduction ratio of Perkins (77) and material balance for multistage washers. These are subjected to computer program C++ and data are generated. The parametric influence is found in close agreement with those obtained from the previous investigators (64,96).

For the estimation of steam consumption in black liquor evaporator system for paper mill as a function of DF and number of stages, the first attempt is made to design a set of multiple effect

evaporator (MEE) consisting of six number of bodies (sextuple effect). This is pursued through designing a cost model with minimum total annual cost as an objective function. This is a single valued non-linear function with N as a decision variable. The profile displayed a unimodal function exhibiting an inflexing point as minima.

The sextuple effect evaporator thus developed, now needed for steady state mathematical modeling. For the present case a typical backward feed sequence is considered. For modeling an analysis is made using degrees of freedom and other standard procedures. Finally a system of 12 nonlinear simultaneous equations are generated based on steady state mass and energy balances, and heat transfer rate equations. The model of overall heat transfer coefficients is taken from Gudmundson (33) whereas the models for physico-chemical/physico-thermal properties of liquor and equilibrium relationships for boiling point rise are so selected from many rival models that they can fit for bamboo and hardwood liquors. Numerical techniques using Newton-Raphson Jacobian matrix and method of Gauss elimination are employed to solve the problem.

A generalized algorithm is developed for the simulation of this backward feed multiple effect evaporator system. Algorithm is also developed to estimate overall heat transfer coefficient based on Gudmundson model. To process a large body of data within limited time and to generate a data bank a computer program has been developed based on Fortran 77. Subroutine-subprograms for the physico-thermal properties of liquor including boiling point rise and overall heat transfer coefficients are also developed to inter-link with main program. Normal parameters practiced in Industry are employed to simulate the system. The influences of various input parameters e.g. the temperatures of saturated steam, feed and last body vapor, feed concentration and flow rate on steam consumption, steam economy and area requirements are examined.

Further, the data bank thus generated for steam consumption and condensate flow rates are statistically analyzed. Non-linear statistical regression models are developed to interlink with

brown stock washing operation as a function of DF and N for further optimization of the later system.

For bleach plant optimization a pragmatic strategy for optimizing a multi-stage bleach plant has been developed. To fulfil the objective a detailed optimization scheme has been designed which is then simulated for a typical bleach plant sequence CEDED as an example. The non-linear models needed linearization, specifying the operating constraints and are solved through linear programming techniques with the help of MATHCAD AND LINDO SOFTWARE PACKAGE. The control set points based on the models are optimized using annual operating cost as decision variable. The total annual cost as objective function has been formulated and simulated with various values of operating conditions such as consistency, temperature, time of reaction, chemicals consumed and final pH within their respective ranges normally followed by industry.

The cost related to ETP required for optimization of BSW operation are usually determined by the quantum of pollution parameters constrained by the pollution control authorities. To examine the effects of carry over solids and kappa number of brown stock, which consumes extra bleaching chemical and generates equivalent COD, BOD₅ and AOX/TOCl in bleach plant effluents, models are developed to predict effluent parameters for various bleaching sequences. The statistical models for various cases are found to be linear, nonlinear (parabolic and polynomial type) for single variable and multiple regressions for multivariable problem. In order to validate the models the experimental data and correlations determined by earlier investigators are compared. The accuracies of the statistical models are further tested through the absolute error, percentage of error, R² values and residual plot.

For estimating heating value of BLS, heat utilized to produce steam and parametric effects on these values a modified version of Green and Grace model and that due to Frederick(22) is proposed after incorporating DF and N terms. Two algorithms and their computer programs using

C++ language are developed to calculate heat value of black liquor solids, steam production from recovery furnace and other parameters. From the proposed model the effect of BLS on HV, which in turn a function of DF and N are evaluated. The effect of sulphidity, active alkali, percentage of BLS on HV and heat utilized for steam generation are examined. These closely agree with those of previous investigators(74,1). Based on the data a regression model of nonlinear type is developed for further optimization.

All the relevant streams from BSW operation, MEE, multi-stage bleach plant, ETP and recovery operation are now converted in cost terms. Total annual cost per tonne of pulp comprising of many cost terms including capital fixed charges together with, power cost of BSW operation, statistical multivariate regression model for steam and condensate flow, carry over of solids and neutralization cost in bleaching operations and heat value of lignin and its impact on overall gain in the recovery furnace are incorporated in the objective function. This is then subjected to nonlinear constraint optimization by Fletcher-Reeves method. Optimum number of stages for BSW and economic dilution factor are thus found out for a variety of conditions. Relative contribution of all cost terms towards total annual cost are evaluated.

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CHAPTER 1

MATHEMATICAL MODELING IN PULP AND PAPER MILL

1.0 INTRODUCTION

Paper industry accounts for nearly 3.5% of the world's industrial production and 2% of world trade. Current annual consumption of paper is of the order of 270 million tonne. This industry is 10th industrial sector in India.

Pulp and Paper Industry is highly capital intensive industry. Capital cost is of the order of Rs.75,000- Rs.1x10⁵ per annual tonne of paper. Indian pulp and paper industry has been suffering from crisis due to scarcity of quality fibers (raw material), high consumption of steam and electrical energy, higher amount of effluent load generation and ecological constraints The industry suffers from a number of uncontrollable factors, the main reasons for high cost are: raw materials are difficult to find or expensive, energy is almost non-existent in some states, chemicals are either expensive, imported or just unavailable.

The major environmental issues associated with pulp and paper industry are deforestation and pollution. Causes of pollution include the nature of processing and the high consumption of materials and energy.

Industry must restructure itself in a manner that it can thrive on these shortcomings. Sustainable growth of this industry needs a closer examination to overcome this crisis as the selling of product has become globally competitive in terms of quality and price. The paper industry (122) is required to improve their operations through new mechanism so that the industry can sustain and survive. As India is a member of WTO the paper industry should be ready to face stiff competition from overseas supplier considering the possible reduction in import duty to WTO levels in coming

years. There are many challenges before Indian pulp and paper industry including ongoing shortage of fiber, vulnerability to price swings in the global market, WTO stipulations, the electronic revolution, environmental issues, the need for state-of-the-art technology, mobilization of financial resources and human resource development.

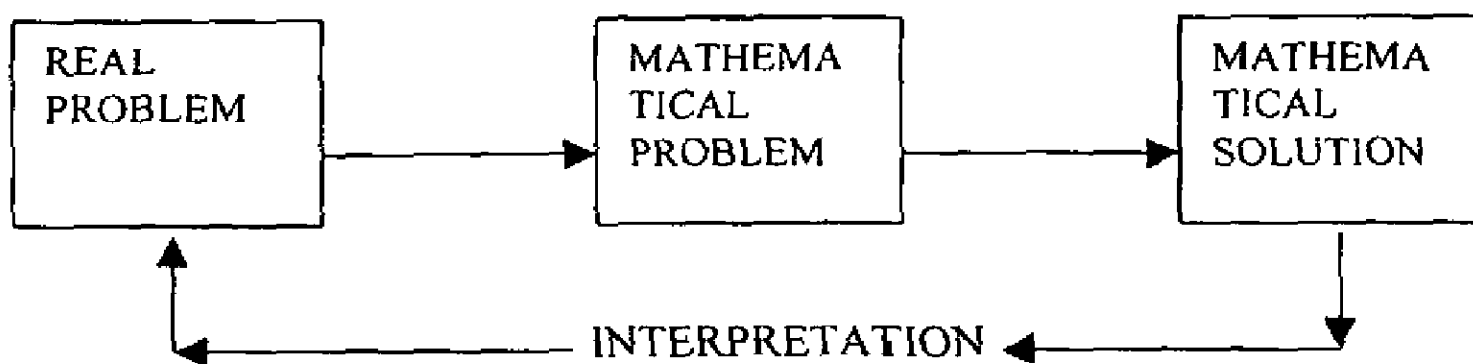
Paper consumption is expected to grow from presently 315 million tonnes to 420 million tonnes in 2010 with Asia as the epicenter of this growth. In India the growth is expected to be more than double by 2010. Therefore, Indian companies will need to invest very heavily to improve quality and productivity, achieve cleaner production and manage fiber requirements in an ecologically acceptable and cost effective way to fight competition from imports.

The foremost task before Indian paper industries for their survival is to develop conceptual system design with sophisticated automation and control which, in turn, require mathematical modeling, simulation and optimization technique for optimizing parameter for both process and plant equipment. However, without mathematical models of the process, optimization can not yield any useful results. Building of mathematical models and their solutions through optimization techniques demand a deep knowledge of mathematical sciences. In the following sections, an overview is presented to show as to how the mathematics interact with industry and help in solving process industry problem to earn the desired profit. Further, the status of pulp and paper mill in India and the raw material, energy- environmental scenario, the concept of washing in brown stock washer (BSW), multiple effect evaporator (MEE) for black liquor concentration, the bleaching of pulp, and the recovery furnace for recovering chemicals with bye-product heat, steam and power generation are briefly described.

However, it is important to discuss before dealing with actual problem how mathematics can help to circumvent the shortcomings. Before developing the model it is imperative to highlight the broad-base view of some related aspects. These are described in the following paragraphs.

1.1 MATHEMATICS AND PROCESS INDUSTRY

For process industry optimization and control, mathematical methods are extremely essential in today's scenario when the globalization has taken place with liberalized economy. Global market with quality product at competitive prices, public awareness regarding environmental degradation, acute shortages of raw material and energy, and high prices of all basic inputs have forced the engineers to adopt design of process, plant and system in a most quantized or deterministic way. The quantification is possible through interaction of mathematics, engineering and physical sciences. Only single factor comprising of preservation of ecology and environment, conservation of energy and resources, recovery and recycle concept has played dramatic role to take the mathematician to solve today's burning problem. The inter-relation between a real problem and mathematical problem can be explained through the following structured block diagram.



1.1.1 Mathematical Methods and Modeling

Mathematical modeling is a mathematical description of both process and operation of a plant. It is used to describe, analyze, correlate, simulate, optimize and finally control an existing or contemplated process. The model must be simple, coherent, less time consuming, must include most pertinent parameters influencing the system, is open to parametric treatment, easily solvable and controllable. Thus this technique is now extensively employed for optimization, simulation and control of a plant through its process and operation and for examining the equipment performance. When the model is ready and well fitted, it can be used for process simulation, i.e. to

evaluate the changes in the effect of some independent parameters on dependent variables. Therefore, mathematical models by nature is classified as: linear or nonlinear, static or dynamic, deterministic or stochastic, discrete or continuous. Steady state model, also called static models is time independent, which needs energy and material balances and can evaluate questions such as the effect of installation of additional equipments or replacement of existing one.

Pulp and paper industry, in fact, has many complex subsystems such as single or multi – stage digestion, brown stock washing, multi stage bleaching, multiple effect evaporation, mud – washing, recovery boiler operation, recausticizing, lime klin and effluent treatment plant to increase its productivity with minimum power, steam, chemical, labour and water usages; there by the severe impact on ecology and environment can be minimized. Therefore, there is a need of sophisticated mathematical techniques to solve the problems of process Industry and estimate the actual requirements of energy consumption and other inputs for its sustainable production. The aforesaid multistage sub-systems generate a number of linear, nonlinear, homogeneous, non-homogeneous, algebraic, ordinary differential and partial differential equations; the solutions of which are sometimes cumbersome, intricate and bewildered. Mathematical methods generally include for solution of the mathematical models by analytical techniques, numerical methods and optimization procedures. There are a number of optimization techniques available for optimal solutions. Generally, there are three major techniques which are frequently used for the optimization of a system i.e. linear programming, non-linear programming and dynamic programming. Some of these techniques must be required in this investigation.

1.1.2 Statistical Modeling

Statistics is also valuable tool for process industry optimization and control where deterministic mathematical analysis is not feasible. In many experimental situations large quantities of information exist in the form of sets of values of several related variables. It is natural in such

situations to seek a mathematical function that tells us how the variables are inter-related. Correlation and regression analysis, analysis of variance (ANOVA/MANOVA), confidence interval and residual analysis etc. are some of the standard statistical techniques to solve industrial problems. The analysis that can be used to examine data and draw conclusions about the functional relationships existing among the variables is called regression analysis. Least square technique is usually used to develop regression models. Many modern statistical methods appear in literature to solve multi-variate problems. It is important to mention here that the present problem by virtue of its nature, invariably demands some statistical techniques. These will be discussed in later sections. The inter-relationship between mathematical analysis and statistical techniques is enumerated below:

1.2 STATUS OF INDIAN PAPER INDUSTRY WITH PARTICULAR REFERENCE TO ENERGY CONSUMPTION, POLLUTION GENERATION AND RAW MATERIALS SCENARIO

As already indicated pulp and paper industry is highly intensive in terms of energy, water, chemical consumption, pollution load and labor.

It consumes approximately 9.5-20 tonnes of low pressure steam, 1300-1950 kWh electric energy, 250-350 m³ of water and generates a pollution load of 300-400 ppm (35-50 kg/t) BOD, 1100-1500 ppm (150-200 kg/t) COD per tonne of paper which are very high compared to Scandinavian and North American mills. Major cost components are: energy=20-25%; raw materials = 20-25%; chemicals=15-20%.

Water consumption and waste water generation are substantial in Indian mills. For each tonne of wood used in paper manufactured by the Kraft process, 42% is recovered as bleached pulp, 4% ends up as solid waste, 5% is burnt in chemical recovery, 5% ends up as dissolved organics in waste water and 2% goes as suspended organic solids.

In Indian paper industry the external fuel sources meet the energy need to the extent of 70% and the rest comes from the surplus net energy available (43) in the chemical recovery process. The fuel component in our paper industry represents as high as 15 to 20% of the total cost of production.

There is an urgent need to circumvent the above problem in order to make the plant sustainable. Recent study indicate that there is growth of this industry worldwide with the increase of the rate of literacy. In India also per capita consumption has been increased within 5 kg approximately. 515 paper mills all over India fulfil the demand of paper. To make it competitive globally it is important to solve many of its inherent problems through mathematical and engineering understanding about the plant. In the following paragraphs a snapshot view of a typical Kraft mill operation is given.

As at present the performance of paper industry is far from satisfactory, the industry must gear up itself for significant improvement in conserving energy attaining optimal efficiency and productivity.

1.3 THE KRAFT PROCESS DESCRIPTION

A paper industry has some major sections: pulping and recovery cycle, stock preparation and paper machine operation, finishing house, effluent treatment plant (ETP). All paper industry in India except one follow Kraft process which is also a dominant chemical pulping process world-wide. The Kraft process uses sodium hydroxide (NaOH) and sodium sulfide (Na_2S) as the pulping chemicals. On completion of the pulping step, the residual pulping chemicals and dissolved substances form an aqueous solution called black liquor. The Kraft recovery system processes the weak black liquor and regenerates the pulping chemicals.

The Kraft pulping process and recovery cycle is illustrated in Fig.1.1 .Raw material preparation and pulping, brown stock washing and recovery cycle consisting of evaporation, combustion,

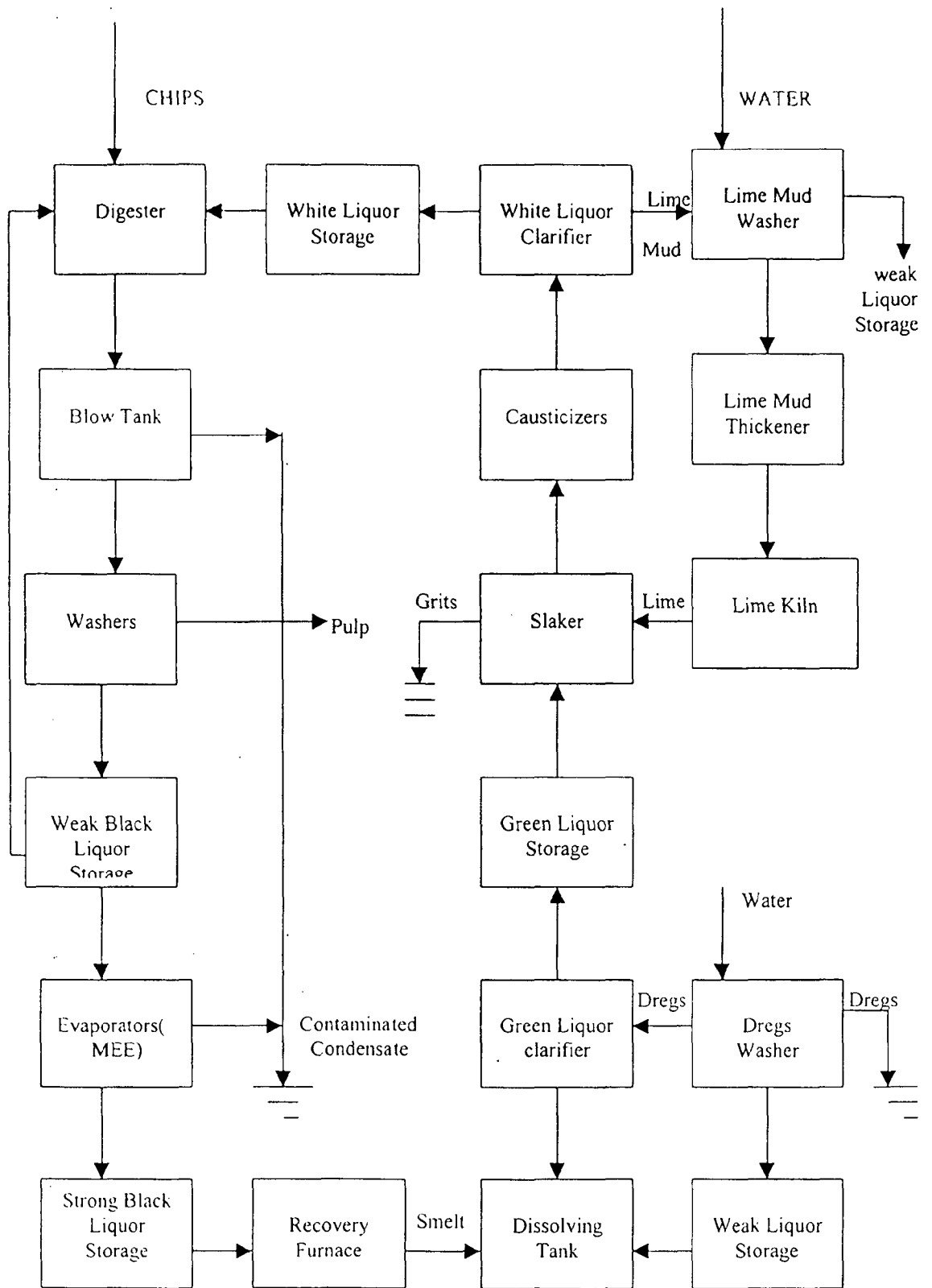


Fig.1.1 Kraft pulping and Recovery Cycle.

causticizing and calcining, bleaching, stock preparation and paper making are the major steps. Generation of Effluents (solid waste, liquid and gaseous) and its treatment are added operation which combines both the recovery cycle and fiber line. Some of the above processes and the pertinent unit operations involved are described in brief in the following sections:

1.3.1 Raw Materials and Pulping

A large number of raw materials containing cellulosic fibers are used for the production of pulps. Majority of Softwoods and some hardwoods are usually employed in North America and western countries. However these raw materials especially softwood (long fiber), are scarce in India though some hard woods like Eucalyptus, Poplar and some other species are in use. Most of the Indian Industry, particularly, integrated mill uses Bamboo alone or a blend of bamboo and hardwood. Small paper mills are mostly using Bagasse, Rice Straw, Wheat Straw, Grass, Sarkanda and others. The quality of fiber depends upon four characteristics: morphological (length, diameter and thickness), anatomical (fibers, vessels, ray –cells, tracheids etc.), proximate analysis (solubility in water, bases, acids and natural organic solvents) and chemical analysis (cellulose, lignin, hemicellulose, extractives and ash). In addition the structure of the chemical components differ widely from raw material to raw material (wood to non-wood, non-wood to non-woods). Because of the nature of the raw materials and their chemical constituents, the pulping processes, the operational parameters, the pulp product quality and the black liquor characteristics (physico thermal/chemical, boiling point rise, viscosity and heating value) are of different magnitudes. Therefore, the design and performance of equipments and process are variant with widely varying raw materials. A typical set of proximate and chemical analysis of some Indian raw materials are depicted in Table-1.1 which shows that the compositions are diverse in nature which in turn affects pulping and other processes.

Raw materials and white liquor ($\text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3$) are reacted in a digester (a pressure vessel) at about 160- 175°C (4.855-9.155 Pressure) to yield Kraft pulp and weak black liquor in bath ratio and around 20% chemical (on BD basis) are used as 110-140 gpl TTA. Some volatiles (turpentine, methanol, reduced sulfur gases) are released.

Table-1.1 A typical chemical composition of fibrous raw materials

Constituents %	Bamboo	Bagasse	Eucalyp.Hybrid
Holocellulose	67.19	73.16	65.80
Alphacellulose	46.58	41.94	45.10
Lignin	24.15	19.37	30.90
Pentosans	19.30	24.10	14.10
Alcohol-benzene extraction	4.19	1.90	1.48
1% NaOH Solubility	28.30	30.23	13.40
Silica	1.40	1.40	0.03
Ash	3.10	1.77	0.44

In this present investigation the data for raw materials like softwood, bamboo and hardwood are used for simulation.

1.3.2 Brown Stock Washing

The objective of pulp washing is to separate the brown stock (pulp) produced from pulping economically recover the maximum amount of weak black liquor with minimum amount of fresh water dilution water to the tune of 2-4 t/t of pulp at about temperature 60-70°C. It is possible to recover at least 98% of the chemicals applied in the digester.

It is important to emphasize that the washing characteristics of pulps differ from raw material to raw material. The specific loading factor (BD fiber production in tonnes per m² per day). For straw pulp is between 1-2 whereas the same for softwood may go upto 5-7. It is necessary to find out the optimum conditions for washing of various raw materials like wood, bamboo, bagasse, straw and grass.

The pulp washing operation consists of simultaneous filtration and mass transfer operation. The basic phenomenon of pulp washing is based on dilution, displacement and extraction. The principle of drum filter washer is illustrated in Fig.1.2 to understand the various unit processes involved in it.

However, the mechanism appears to be complex due to the presence of diffusion, dispersion, adsorption-desorption, foaming and incomplete mixing. During the washing process mass transfer is involved between the wash liquor and the stagnant liquor within the cake pores.

In industry some parameters are defined that can be classified as wash liquor usage parameters (e.g. DF), solute removal parameter (e.g. DR) and efficiency parameters (EDR, E_{st}) to quantify the performance of BSW.

The black liquor is diluted by the wash water which is usually expressed as dilution factor (DF) or excess water per tonne of pulp. This is the difference between the water applied as wash water in the last washer and that portion of the wash water that is discharged with the pulp from the last washing stage. DF can be mathematically expressed as follows:

$$DF = (W_S - W_L) / W_P \quad (1.1)$$

There are another important parameter required to express the washing efficiency, called displacement ratio (DR). DR is defined as follows

$$DR = (X_0 - X_1) / (X_0 - X_2) \quad (1.2)$$

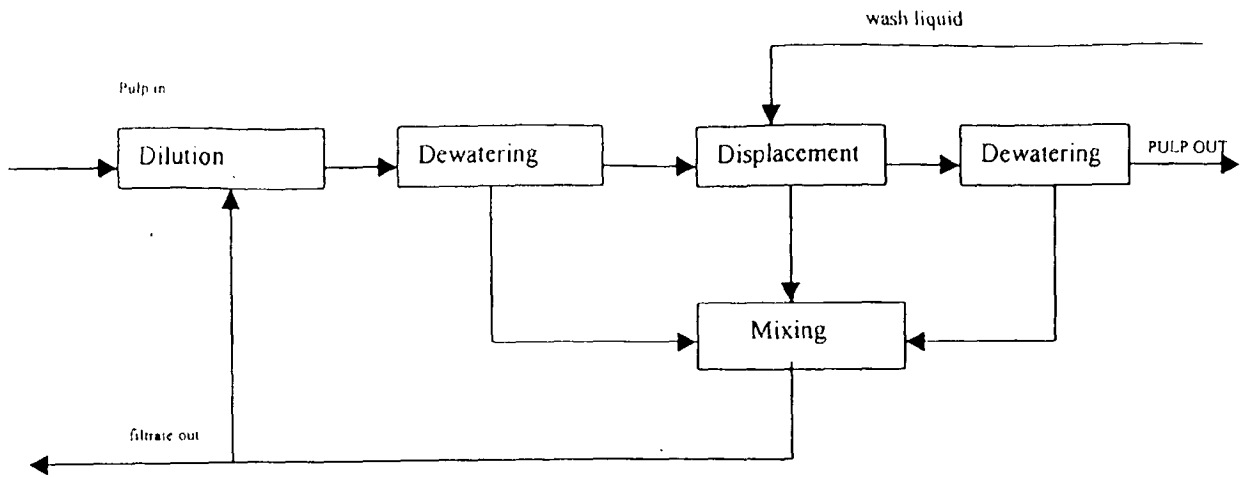


Fig. 1.2 A Block Diagram of a Simulation Model for a Drum Filter Washer.

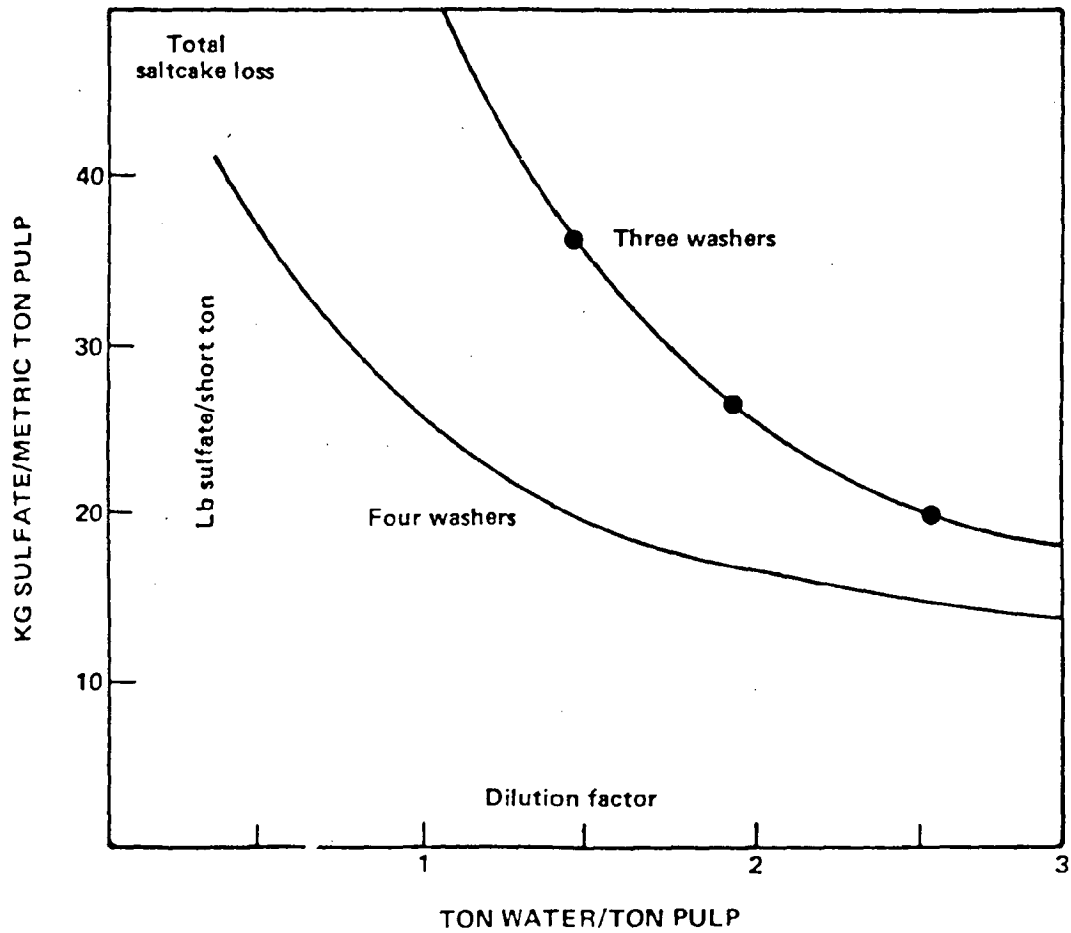


Fig. 1.4 Relationship Among Salt Cake Loss, Dilution Factor and Number of Washers.

Another important parameter is washing efficiency of BSW. If industry data is available it can be defined as

$$\%WE=100/SCC (SCC-SCL) \quad (1.3)$$

$$\%WE=(1-DR_1)(1-DR_2)(1-DR_3)\dots\dots(1-DR_n) \quad (1.4)$$

Important parameters required to estimate the capacity of the washer are area (A), permeability (k), fractional submergence (μ), fiber production rate (FPR) etc. These are reported by Tyagi (117) and Kukreja (55).

Different type of equipments used for Brown stock washing are: rotary vacuum washer, pressure washer, digester washer, wash press, screw press, belt washer, diffusion washer, atmospheric diffusers and fiberfuge washer etc.

Of all these equipments, rotary vacuum washer is the most versatile, simple in operation and design and is very commonly used equipment in the industry globally. In industry a battery of 3 to 4 rotary vacuum washers connected in a counter current manner is used to wash the pulp using wash water at 60-70⁰C.

A sketch of rotary drum filter is shown in Fig.1.3 (55). A typical set of detailed design specification is given in Table-2.3 of chap-2. It consists of Cake formation zone, first dewatering zone, washing zone, second dewatering zone, blow and discharge zone and finally dead zone.

Basically all vacuum drum washers operators under the cycle as shown in Fig.1.3. Stock at 0.75 to 2.5% O.D. consistency is fed to the inlet box of the washer and overflow the weir into the vat containing counter rotating cylinder or drum (97). The drum has a filter media generally a mesh cloth of plastic or metal between 25 and 40 mesh called the “face”. The “face” is installed on the periphery of the drum, and is supported by a substructure which is different in design depending on the manufacture of the washer drum.

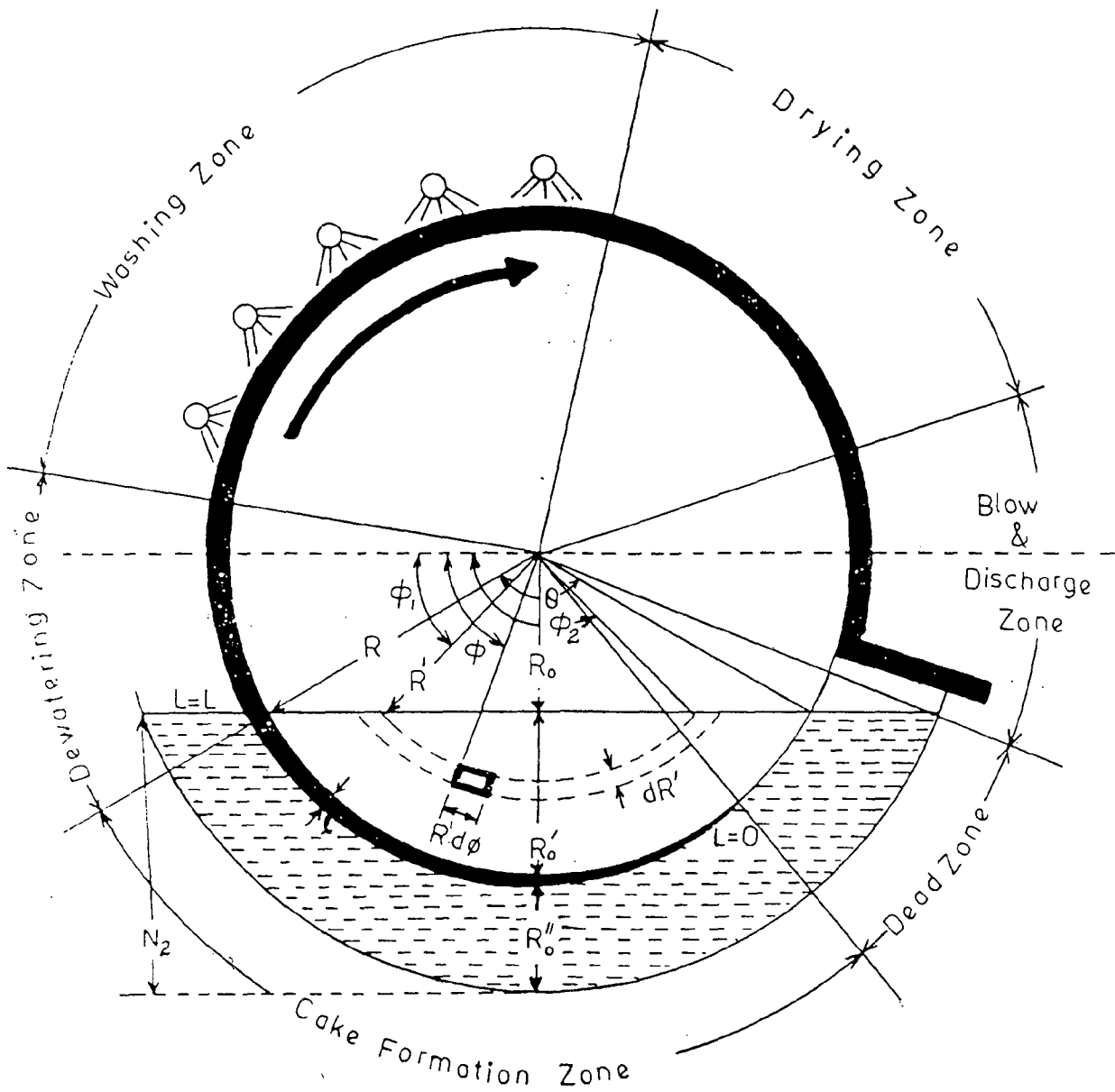


Fig. 1.3 Different Zones of a Rotary Drum Filter.

A vacuum is drawn on the interior of the drum, generally developed by a drop leg or by a vacuum pump, which forms the driving force for extracted liquor from the pulp slurry. This drainage of liquor results in the formation of a pulp mat on the drum in the sheet formation zone. As the sheet emerges from the slurry in the vat, liquor is further extracted by the pressure differential as it moves into the displacement washing zone. Fresh water or recycled liquor is applied to the formed mat generally through distribution in multiple shower pipes. This wash liquid displaces the liquor in the sheet, after which additional liquor is extracted in the dewatering zone. When the rotary vacuum washer is a part of a multistage system, the cleanest wash water is applied at the showers of the final washer. The effluent from the cylinder of the final washer is then used to dilute the pulp entering this washer and on the showers of the previous washer. The effluent from the previous washer is directed back in a similar manner countercurrent to the pulp stream.

At the point where the pulp mat is removed from the drum, the pressure differential is eliminated so that the sheet can be continuously discharged from the drum. The mechanism for the elimination of the pressure differential varies widely depending upon the drum design used, but typically involves the use of a valve which cuts off the drum face from the vacuum.

Pulp is discharged from the washer drum at the 8 to 18% O.D. consistency depending upon washer and auxiliary equipment design, as well as pulp drainage characteristics and operating procedure from the drum. As an example the pulp is to be processed at dilution from around 15% consistency to 2% at the vat, dewatering to 10%, a displacement washing at 10% followed by final dewatering to 15%.

A pressurized drum washer also operates in accordance with these principles but includes additional steps such as compaction of the formed pulp mat.

As evident from the literature that to wash commercial pulp in industry there are certain designs and accessories which play dominant role for efficient operation. These are: drop leg /barometric leg

design configuration, its height and diameter, filtrate volume, the velocity of flow of filtrate a volume of air and the filtrate tank design to eliminate air and for submergence of drop leg pipe seal tank. The exact values of the design parameters depend upon the size and the dimension BSW. These are reported by Perkins (76).

Table-1.2 Design parameters of BSW system

Dropleg height	9.144-10.668 m
Velocity	2.7432-3.6576 m/s
Height of seal tank	6.096 m

Industry uses following assumptions as thumb rule to get better performance. These are: low submergence, long washing, and drying cycles, short blanket area, low liquor velocity, low nozzle pressure, uniform wash liquor distribution, uniform fiber mat thickness. It is also tacitly assumed that the optimum wash liquor temperature is between 60-70⁰ C with inlet and outlet consistency as 1% and 16% respectively. It is not known exactly that how variation of liquor velocity, blanket thickness, pulp pad consistency, temperature initial liquor concentration and wash water concentration change washing performance. The number of stages and the dilution factor or water usage have balanced by trial and error means. Therefore, there is an inherent trade-off in industry between solids recovery and dilution.

To recover these chemicals, the water used for washing must be evaporated.

In actual practice multi-stage BSW (3-4 stages) are generally used and worked in countercurrent manner. It is a fact that higher the number of stages, higher is the cleanliness of pulp. This is shown in Fig.1.4 which indicates that the soda loss is less in higher number of effects. A typical sketch of three stage washer is shown in Fig.1.5.

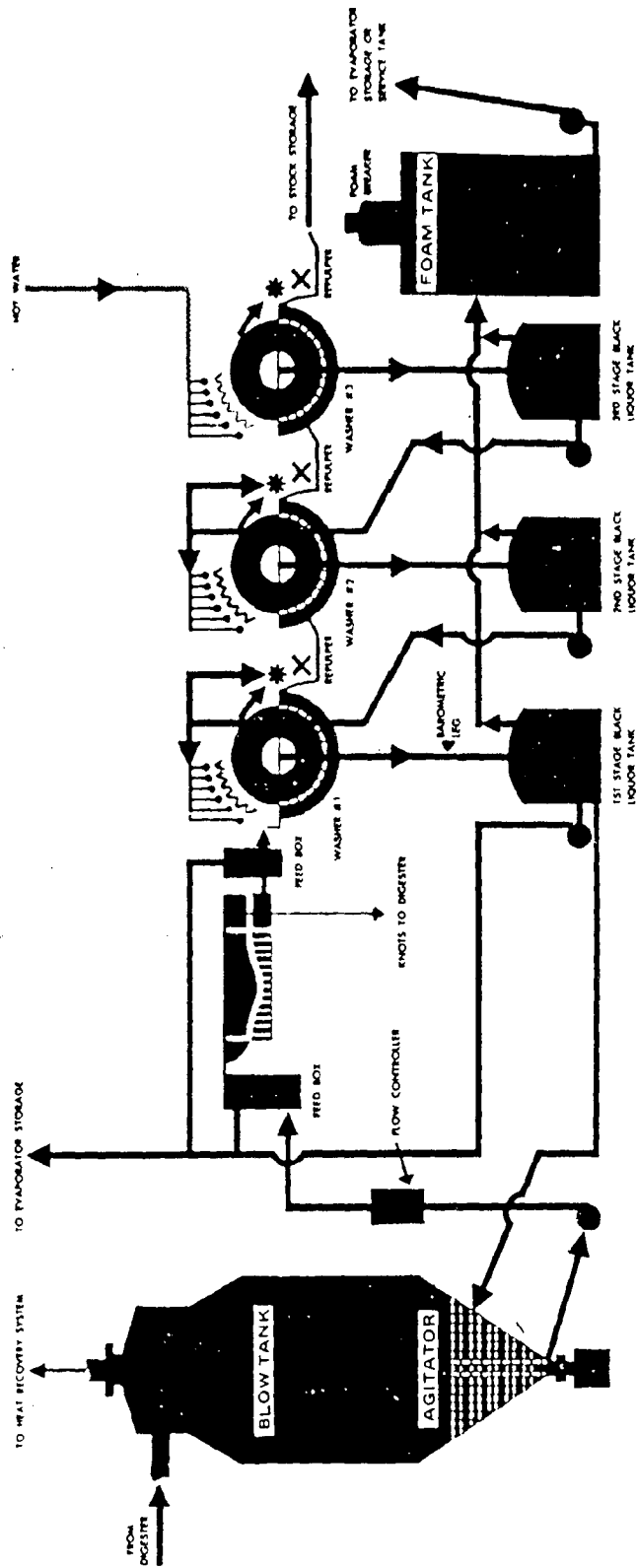


Fig. 1.5 Schematic Diagram of Three Stage BSW.

Presently the knowledge on the pulp washing plant is mostly empirical. The design and operating procedures for the washers have evolved from the experience gained over the years. Due to the limited supply of raw material, high chemical cost and tight pollution regulations, it is necessary to find out the optimum conditions for washing of various raw materials like wood, bamboo, bagasse, straw and grass.

It is not known how many stages and at what dilution factor the operation works optimal. Therefore, there is enough scope to investigate these parameters in actual working condition in an Indian mill. In the present investigation therefore effects will be made to find out some of the factors related to both design of equipment and operation.

1.3.3 Bleaching

In a bleach plant the pulp from brown stock washer is subjected to bleaching action to enhance brightness without any detrimental effect on yield and strength. The bleaching process consists of three steps namely bleaching, particle removal and brightening. In a bleach plant, bleaching of pulp usually takes place through several unit processes and operations. The processes are connected with many chemical reactions depending upon the nature of oxidizing (oxidative bleaching) or reducing (reductive bleaching) or enzymatic agents applied to the pulp. For chemical pulp bleaching the oxidizing bleaching agents are used. These are: Cl_2 (C), ClO_2 (D), sodium Calcium Hypochlorite (H), Peroxide (P), Oxygen (O) Ozone (Z). The stages also need alkali in the extraction stage, denoted by E. The chemical reactions or the biochemical reactions (in the latter case) are very complex. The reactions also are of many types: principal and side reactions. The operations involved to perform the task of bleaching needs single or multistage bleaching sequences, though the latter is almost invariably used throughout the world except in very few cases of pulp like those of non wood based pulp depending upon the brightness desired. The operation normally is accomplished in a series of equipments like mixer, retention towers, washers

and a couple of pumps for pulp slurry transportation. The operational parameters are: consistency of pulp, temperature and time of reactions, dosages of chemicals, the concentration of the residual chemicals and the final pH. Most difficult point is that chemical reaction in each stage demands different conditions of the above parameters.

The color of unbleached pulps is predominantly caused by the lignin remaining in the fibers after pulping. Consequently, the bleaching process is designed to react with lignin, either to remove it or to convert to a colorless form. The former approach is taken with Kraft pulps, while the latter one is applied to mechanical pulps.

In multiple-stage bleaching processes, like CEH -the three steps are repeated in a sequence. The need for multiple-stage bleaching arises from the fact that the removal of too much lignin in any given bleaching stage will degrade pulp fibers causing shrinkage and lower their strength. Thus, lignin must be removed a little at a time so as to minimize undesirable side reactions with pulp fibers.

For optimization it is very difficult to do for all these processes because of uncertainty of chemical kinetics and non-availability of appropriate model. In this present investigation, therefore, known models are used with CEDED sequence shown in Fig.1.6 though CEHH, CEHEH, CEHDED, CEHED, CEHDHDP, CEHEDP, CE₀DED, C/DEDED, CE_pDED, CEOPDED, etc. are other sequences used in pulp and paper industry. Though CEH is the simplest multiple stage sequence, it has become outdated because of more demand of brightness for quality paper. In this present study, CEDED is chosen because of its wide acceptance worldwide to provide high brightness with little damage to the pulp at a reasonable cost (30). It has been reported that 31% of Swedish pulp and paper mills and 38% in North American mills are using this process.

problems. Depending upon the evaporator capital cost based on present market price, the number of units in the set-up of MEE, and the steam cost, a minimum cost design can be determined. In majority of cases the number of evaporator bodies in a paper mill is even limited to 5, though four effect MEE is not completely out of practice in Indian mills.

Evaporator is in fact, one of the largest energy consuming stages in a paper mill and around 24 to 30% of the total steam input is consumed in this section. North American mills producing bleached pulp have reported to consume 25% of the all steam generated or approximately 20% of the total mill energy requirements. This might be partly due to differences in evaporator designs.

In India and surrounding countries the practice of concentrating the black liquor upto 45-55% (typically 50%) in the evaporator section is still existing, because of other problems due to different raw materials (Bamboo, Hardwood, Bagasse and straw etc.) and transportation problem to the recovery section. It is well known that as the solids are increased by evaporation of water in the evaporation plant, the black liquor becomes more viscous and its boiling point rise will increase disproportionately resulting in loss of capacity. This is of extreme importance in the context of Indian raw materials. Therefore as indicated earlier Bamboo/Hardwood are mostly used in Indian mills, attempt will be made to evaporator modeling with this liquor.

The higher steam consumption or poor steam economy in the evaporator section of Indian paper industry is the resultant of many factors connected with the operation and design of the multiple effect evaporator system (long tube rising film, short tube and falling film) and not limited to only raw material species and quality variation.

Though falling film (FF) type is the latest trend abroad, in India still long tube vertical (LTV) is the overwhelmingly predominant design except for a very few mills. LTV has advantages for providing higher throughput capacity (compared to short tube vertical called STV) per unit area,

can be adopted easily to forced circulation system and other operational conditions. Besides, LTV is used globally because of its flexibility in operation and based on relatively known mathematical analysis. Therefore, it will be of immense help to the designer and operating personnel of paper industry, especially in India if thorough investigation is made with LTV. Indian industry will also be highly benefited if immediate attention is paid to analysis of LTV system. A typical sketch for LTV is shown in Fig.1.7.

The energy economy also influenced by the liquor flow sequence of MEE and liquor characteristics. Multiple effect evaporators may be arranged in a variety of ways. Forward feed, backward feed, mixed feed and parallel feed are the four general types. Parallel flow has its own limitation for black liquor concentration. Due to very high viscosity of the strong liquor having higher concentration and their non-Newtonian characteristics, it becomes difficult to process in a forward feed sequence which obviously poses operational difficulties.

The liquor flow sequence in a black liquor evaporator should be designed to give the highest possible capacity per square meter of heating surface consistent with the high steam economy. North American evaporation plants generally employ a 5-6-4-3-2-1 or 6-5-4-3-2-1 liquor flow sequence and the weak liquor is fed to the last (5th or 6th) effect with steam flow sequence 1-2-3-4-5-6 with an aim to achieve slightly higher capacity (slightly lower economy) compared to other configuration (43).

As a result, the design is mostly of backward flow type. Literature is also available which indicates that backward feed usually results in the best overall economy (balancing both capacity and steam economy, defined as vapor generated per mass of externally supplied steam) and therefore is most commonly employed (58) though Perry (79) referred that mixed feed is used only rarely but in practice due to high cost of electrical and steam energy, industry is switching over to this type of

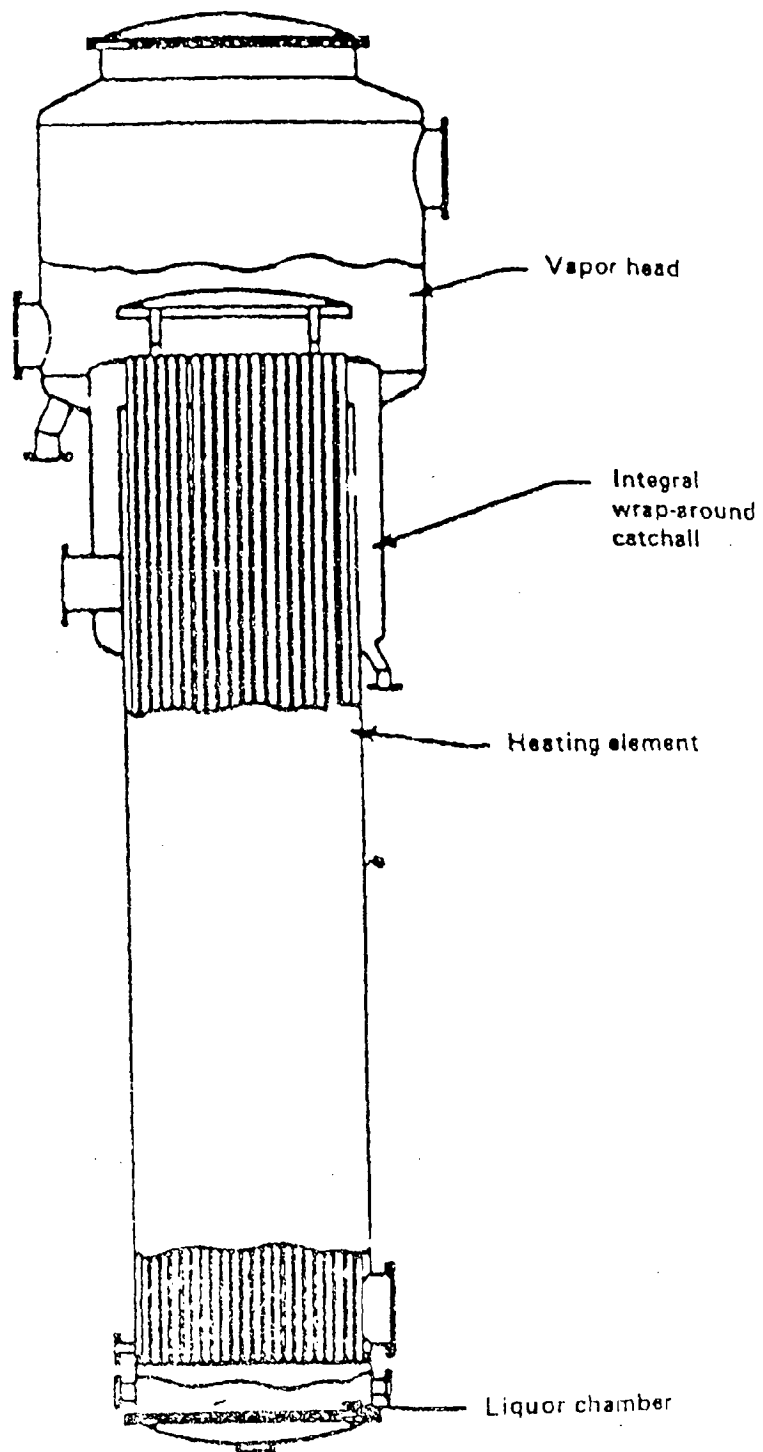


Fig. 1.7 A Typical Figure for LTV Evaporator.

feeding sequences from truly backward feed sequence which had invariably captured the market over more than fifty years due to its advantage in terms of higher capacity.

From the above description regarding MEE, it is quite clear that one has to know the following for complete modeling of the process.

- Type of the liquor processed in an Indian paper mill as the operation is highly influenced by the nature of the liquor to be concentrated, its physico-chemical and physico-thermal properties and overall heat transfer coefficient values. Bamboo and Hardwood liquor should be one's prime objective as they are predominantly used by Indian mills.
- The optimum number of effects in MEE set.
- The evaporator design configuration(LTV, STV, FF)
- The liquor flow sequence

1.3.5.2 Combustion

The Kraft recovery system has three functions:

1. Recovery and reuse of the inorganic pulping chemicals (most important).
2. Removal and sale of valuable organic by-product chemicals which do not play a critical role in the economic viability of the Kraft process.
3. Destruction of the remaining organic material and recovery of its energy value as process steam and electrical power (important).

Concentrated black liquor (50%) from evaporator plant is further concentrated in a direct contact evaporator (DCE) using the flue gases from the recovery boiler or through a concentrator up to 60-70% solids (typically 65%) before burning in a large unit called recovery furnace. This liquor used for firing is usually referred to as heavy black liquor (HBL). As indicated the black liquor solids release heat when it burns in the recovery boiler furnace. A typical sketch of the operation is shown in Fig1.8. The objective is not only to complete the combustion of the organic matter in

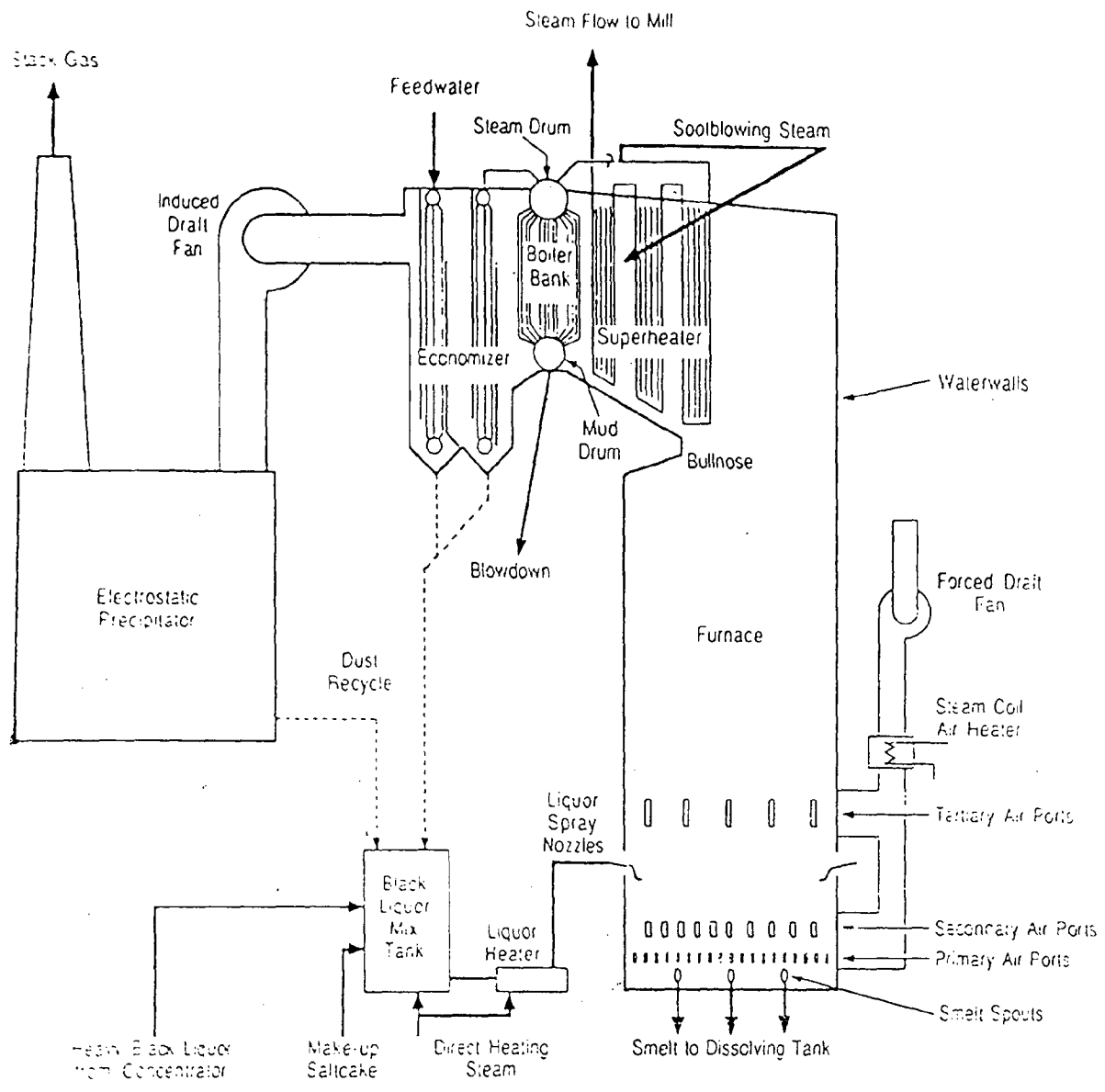
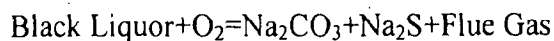


Fig. 1.8 Schematic Diagram of a Kraft Recovery Boiler.

black liquor, but also to recover the sodium and sulfur content in a form suitable for regenerating the pulping chemicals. The overall combustion reaction can be represented as:



The formation of Na_2S requires a local deficiency of oxygen. This “reduction step” is critical. The only part of the recovery cycle where oxidized sulfur compounds can be converted to sulfide is during combustion. The inorganic compounds melt flows out of the furnace as a mixture of molten salts called smelt.

High-pressure steam when passes through a turbine electrical power is generated and the process steam is extracted from the turbine at lower pressures and is used for process heating in the mill, especially for digester, MEE and paper machine.

The recovered energy efficiency (thermal efficiency) of the boiler is about 65%. The calorific value of black liquor dry solids varies from 13490 to 15350 kJ/kg based on softwood liquors which will produce in a modern recovery boiler approximately 5400-6400kg of steam/metric tonne of pulp. However in actual practice in India these values can be miserably lower to even 50%(both in calorific value and steam generation rates) because of raw materials quality and their variation.

Recovery boilers have two main sections: a furnace section and a convective heat transfer section. All mixing and combustion of the fuel and air should be completed in the furnace section as well as about 40% of the heat transfer from the combustion gas. Heat transfer to the boiler water to from high pressure steam is then completed in the convective heat transfer section. The bullnose shown in Fig. 1.8 is the general demarcation between these two sections. In the figure it is seen that some salt cake (Na_2SO_4) is to be added as a make up which are lost as soda losses during washing in Brown stock washer. More is the loss; more has to be added in the recovery furnace. Generally 45-50 kg is required per tonne of pulp. A set of typical data per tonne of pulp is shown in the following Table(Table-1.4 (based on 1.5 t BLS is equivalent to 1 t of pulp)).

Table-1.4 Typical data per tonne of pulp

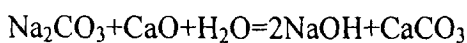
Input	Per tonne	Output	Per tonne
Heavy black liquor(65% solids)	2.3 t	Smelt to dissolving tank	669 kg
Make up salt cake	45 kg	Steam flow to mill	4.851 t
Humidity	102 kg	Blow down	270 kg
FD air	7.24 t	Stack gas	10.0 t
Infiltration air	615 kg	-	-
Dust recycle	90 kg	-	-
Soot blowing	30.9 kg	-	-
Feed water	5.43 t	-	-

Ports are provided for introduction of air, the liquor guns, and other openings such as fossil fuel burners, entry doors and inspection ports.

1.3.5.3 Causticization

The smelt leaving the furnace is dissolved in water to produce a solution called green liquor. The main components in green liquor are Na₂S (obtained by reduction of salt cake) and Na₂CO₃ and a small amount of NaOH. As the green liquor contains some impurities, the green liquor is clarified and causticized with lime to produce white liquor which is recycled after clarification for pulping.

The reaction is



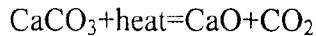
The CaCO₃ is insoluble in white liquor and is removed as lime mud.

This is recausticized and washed in mud washers to remove entrained white liquor and then sent to mud filters.

1.3.5.4 Calcination

The weak wash liquor from filter is sent to the dissolving tank. The washed mud is then calcined in a rotary limekiln or fluid bed calciner to regenerate lime by providing heat from oil or natural gas.

The calcining reaction is



(Lime Mud) (Lime)

The resulting lime is used for causticizing and the calcium cycle is complete.

Calcining is a high-temperature, heat –absorbing (endothermic) reaction. The calcining temperature is about 871oC and the heat of reaction is 3221.15 kJ/kg lime (CaO). The total energy required ranges from 6.86 to over 10.56 million kJ/tonne lime.

1.4 INTERACTION OF BSW OPERATION WITH OTHER PROCESSES

The multiple effect evaporator plant has been considered in the previous section as a single unit operation in the chemical and heat recovery process of the alkaline pulp mill. However, the input and output streams in this system, such as the feed black liquor, steam, condensates, vapors, and concentrated liquor all have an important impact on the operation of the entire pulp mill. Critical aspects of the interaction of the evaporation plant with the rest of the bleaching and recovery processes are needed to discuss in the following sections. Where bleaching is to follow, a tightly controlled washing reduces the need for bleaching chemicals and makes for a more stable bleaching process.

As already indicated, an important process variable determining washing efficiency is the washer dilution factor. The wash water used increase the dilution of the black liquor decreasing its concentration, obviously imposing an additional load on the evaporation system. The need to balance high brown stock washing efficiency reducing soda loss against steam costs involved in

evaporating the added wash water has been addressed by many investigators (43). The salt loss with washed pulp decreases as the dilution factor is increased. More generally, the salt loss can be reduced by increasing the dilution factor, reducing the washer loading, or by installing a greater number of washing stages. The following Table-1.5 indicates the effect of DF on soda loss and black liquor solid concentration for a typical bamboo based 250TPD mill with three stage washers. As the concentration of dissolved solids in weak black liquor depends upon pulp moisture, pulp yield, white liquor strength, bath ratio, washed pulp consistency, digester type (batch or continuous) steam supply in digester (direct or indirect) and blow steam recovered, conditions should be specified for such a complex system during optimization and simulation. It is generally found that continuous digesters give 2-3% total solids higher liquor concentration compared to batch units under similar pulping conditions.

Table-1.5 Soda loss and BL, % solids for various DF for a typical bamboo based mill

DF	Na loss as kg Na ₂ SO ₄ /t of pulp	Black liquor solids, %	
		Direct steam	Indirect steam
2	20	17	20.3
3	18	15	17.7
4	17	13.5	15.6

(Chip moisture=40%; Pulp yield=50%; White liquor strength as Na₂O, gpl=90, Liquor to wood ratio=3.5%, Liquor to Wood ratio=3.5:1, Consistency of washed pulp=12%)

It has been shown graphically (43) the relationship among dilution factor, salt cake loss and evaporation cost. For each mill there is an optimum (economic) dilution factor which generally varies between 2.5-4.0 (43) for three stage washer. Though 4.4-5.4 m³/BDP at a temperature of 6

70⁰C has also been reported by Bjorn and Gren (11) In recent years rising energy cost and environmental constraints have justified the addition of a fourth or fifth washer stage to minimize salt cake loss to less than 10 kg/metric tonne pulp at dilution factor below 2.5. Lowering the washer dilution factor, will, of course, raise weak black liquor solids and reduce steam use for evaporation needs.

The washed pulp is decolorized in the bleaching plant. The solutes present in entrained liquor in pulp are mainly Na and lignin based. Higher the amount of solute present in the pulp, higher is the bleach chemical consumption. Hence quantum of pollutant components is formed in the bleach plant effluent in terms of chloro lignin, AOX, TOCl etc. On the other hand permitting more solute with the pulp gives a liquor of less energy value. Minimizing carry over of black liquor solutes by the pulp can be accomplished by using more wash water. In this case COD, BOD will decrease, but fixed charges, repair, maintenance and cleaning charges and power cost will increase. Hence it is very much necessary to find out the optimum operation of brown stock washer to reduce pollution load in pulp and paper industry. Thus the present proposal intends to envisage vast industrial applications.

1.5 CONTROL STRATEGY FOR BSW

The purpose of automatically controlling a brownstock washing system is to minimize the effect of process disturbances on the removal of dissolved solids from the pulp. The benefits include a reduction in production costs and environmental loading, and the possible improvements in product quality and mill capacity. Most washing plants are still controlled manually however, due in part to a lack of sensors to monitor the process continuously. Automatic control of brownstock drum washers has been limited primarily to low-level control loops.

Many investigators (70,116,125) have reported several control schemes, most of them are based on optimum DF i.e. maximum cleanliness of pulp with minimum use of water and minimum loss of

chemicals without any excursion of the process. One of such control strategies designed by Turr (116) et al. is shown in the Fig.1.9. This employ combination of feed forward and feed back control. This control strategy appears to be an accurate, simple, real time control system for optimal washing of pulp. The above strategy clearly dictates that the optimum value of dilution factor or shower water flow rate is essential which can be manipulated to offset the effect of process disturbances on a washing system. The large and instantaneous effect of the shower water on the removal of dissolved solids in the washed pulp stream simplifies the design of a good control scheme.

Therefore, it is very important also from control of plant to find out the optimum dilution factor and the optimum number of washing stages.

Keeping the above considerations in view present investigation is planned to critically analyze the brown stock washer in details with the following distinct objectives.

1.6 DEVELOPMENT OF MODEL FOR OPTIMIZING BSW

It is evident from the literature that as modeling of pulp washing system has become a valuable method for a wide range of applications including control, process design, troubleshooting and performance check of operating plants. In the present study the following strategy has been adopted from phenomenological point of view.

1.6.1 Review of Optimization of BSW

1.6.1.1 Development of Models for multi-stage Brown Stock Washing

The mathematical models for multi-stage washing plant, multiple effect evaporator, multi-stage bleaching, heating value of black liquor calculations in recovery furnace and the impact on the effluent treatment plant are required for optimization of BSW. Sufficient literature is available on the fundamentals and development of models of brown stock washers, their solutions and theory of

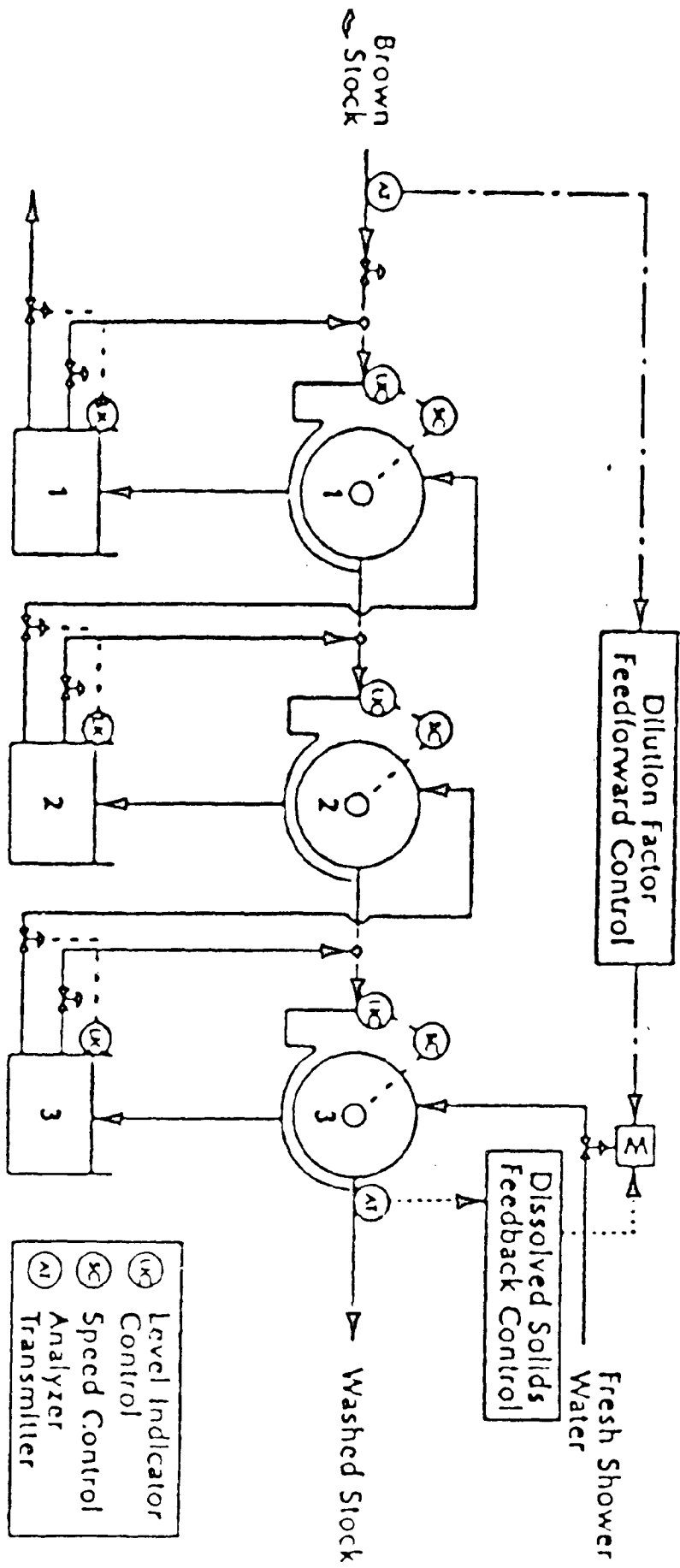


Fig. 1.9 Control Strategy for Brown Stock Washer System.

filtration (55,85) either in steady state or for transient conditions for control purposes. However, the information regarding optimization through cost models are scarce.

The optimal dilution factor has been graphically shown by Sande et al. (93), Woodard (125) Korhonen (54) and documented by Gerald (43) where annual cost per tonne of pulp has been plotted as dependable variable. But no mathematical formulation has been reported. Mahapatra et al. (65), Kamran et al (49), and Singhal et al. (100) in these reports, have also shown graphically the value of optimum dilution factor for a known number of stages. No analytical model is derived there too. In all the above cases, the number of stages are limited to three only. Mathematical problem therefore needs the cost models of all interactive operation affecting washing plant.

On the Multiple Effect Evaporators, modeling and simulation of the systems, physicochemical and transport properties and design methods have been dealt with by many investigators (33,79,87,88,98). However, the knowledge on cost optimization related aspects and mathematical programming solution are limited. Ray (88,98) developed the detailed annual cost model for forward feed sugar juice evaporator with low boiling point rise. Ray, Rao and Ghosh (88) discussed regarding optimum number of effects for black liquor concentration. But these are basically for optimizing the system using simplified methods. Literature (32) is also available regarding the methods for estimating higher heating value of black liquor solids. There have been considerable research on multistage BSW control (70,94,125) in actual plant but all these works do not include the interaction with washing operation.

Not much work has also been reported on the mathematical approach to solve the problem of optimization of brown stock washer combined with evaporation in multiple effect, effluent treatment plant the bleaching sequences, the recovery operation and It does not refer how dilution factor (DF) and number of stages (N) can be optimized in a system with complex interact

among multiple operations. Thus there is ample scope to investigate the overall effect of evaporation, bleaching and lignin utilization on the optimization of multiple stage brown stock washer. Hence there is in need of development of a cost model of all the above interactive operations in order to optimize bleach plant.

1.7 OBJECTIVES

1. To formulate an objective function for cost optimization of brown stock washer of N number of stages as a function of dilution factor (DF) and to select various steady state models for evaluating some cost contributing factors relating to operational and design parameters of BSW.
2. To develop algorithms for static models of single and multiple stage brown stage washer in terms of material balance, solid reduction ratio and displacement ratio.
3. To examine the interactions of dilution factor with the process and design parameters for single and multistage washer.
4. To develop total annual cost model to find out the optimum number of effects of multiple effect evaporator for black liquor concentration with a computer program.
5. To develop a steady state model for N effects (as determined in step 2) backward feed long tube vertical rising film evaporators without flash based on material balance, energy balance, and heat transfer rate equations using appropriate relevant physico-chemical/thermal and transport properties of Bamboo/ Hardwood black liquor and the model for the overall heat transfer coefficient developed by Gudmudson (33).
6. To develop a procedure to solve nonlinear model (developed in step-3) for multiple effect evaporator using numerical method and a computer program for this design along with many subroutine subprogram for the parameters as explained in step-3.

7. To design a statistical multivariate linear/nonlinear regression model for estimating steam consumption/condensate saving as a function of DF and N as required in step 1 for further optimization of BSW.
8. To develop an objective function for minimizing the total annual cost of operation of a generalized bleach plant using CEDED sequence (as a typical case) and also separate models for each stage as constraint.
9. To find out the optimal parameters of step 8 by linear programming using computer softwares.
10. To develop multiple regression model for estimating effluent parameters such as AOX, COD, BOD, TOCl, etc. of bleach plant in terms of chemical consumption, kappa number and carry-over solids from washing plant as required in step-1.
11. To develop a mathematical model using material balance and chemical reaction engineering principles for calculating the neutralization cost in bleaching for various dilution factors and number of stages and to examine the impact of cost due to effluent treatment on BSW operation (in step 1).
12. To develop a model for calculating the heat value of black liquor solids in recovery operation for various dilution factors and number of stages as required in step 1 and to develop regression models based on computed values from algorithm developed in terms of dilution factor and number of stages of BSW.
13. To identify the optimal dilution factor and number of stages of BSW with the models for the cost parameters at optimized conditions of MEE, multistage bleach plant, recovery furnace and effluent treatment plant described in step-1 by non linear programming with constraints developed and to suggest a control algorithm for optimal operation as concluding remarks.

To fulfil the above objectives a number of algorithms are required to develop based on various steady state static models.

1.8 DEVELOPMENT OF OBJECTIVE FUNCTION

The objective function of multi-stage bleached plant can be formulated as follows:

Total cost of washing (C_T)=Cost of washing Equipment (P_w)+Cost of maintenance and repair (P_M)+Cost of power due to drum rotation, back shower pump, vacuum pump, ($P_o * C_{13}$)+Cost of power for repulper-shredder ($P_o * C_5$)+Cost of evaporation ($P_E * C_E$)+Cost of steam for hot wash water ($P_A * C_A$)-Cost of steam generated due to heat value of BLS ($P_E * C_L$)-Cost of condensate saving ($P_s * C_s$)+Cost of bleach chemicals due to carry over solids ($P_{NB} * C_{NB}$)+ Cost of power due to liquor spray ($P_o * C_6$)+cost of power for screw conveyer at last BSW($P_o * C_4$)+Labor cost(C_{LW})+Cost of effluent treatment($P_{Eff} * C_{Eff}$) + cost due to soda loss($P_{sl} * C_{sl}$)+ cost due to total solid loss($P_{tsl} * C_{tsl}$).

$$\text{Min } (C_T) = (P_w + P_m) * N + P_E * (C_E + C_A + C_L) + P_s * C_s + P_{NB} * C_{NB} + (C_{13} * N + C_5 * (N-1) + C_6 * N + C_4) * P_o + C_{LW} + P_{Eff} * C_{Eff} + P_{sl} * C_{sl} + P_{tsl} * C_{tsl}. \quad (1.5)$$

Where C_{13} = power consumption due to drum rotation (C_1)+ back shower pump (C_2)+vacuum pump (C_3).

1.8.1 Strategy for optimization

For cyclical relationship among various operations it has been felt necessary to develop various statistical multivariate linear/nonlinear regression models for estimating effluent parameters of bleach plant in terms of chemical consumption, kappa number and carry- over solids from washing plants, for estimating steam consumption, condensate saving, steam generation due to heat value of black liquor solids as a function of dilution factor and number of washers. To identify the optimal dilution factor and number of stages techniques of non linear programming with constraints can be attempted.

Now, one has to evaluate all the cost contributing terms from respective operations one after another in sequence, namely multi-stage washing, MEE, recovery operation, bleaching and

effluent treatment. Each of the operations need development of mathematical models, the solutions and parametric effects. These are, in fact, required to interlink each operation optimization. These are given in subsequent chapters.

1.9 CONCLUSION

In this present investigation mathematical models are attempted for optimizing a multi-stage washing plant. Accordingly an objective function has been formulated based on minimum annual cost. As this objective function involves terms related to other two important operations such as multiple effect evaporator and multi-stage bleaching along with usage of heating value of bleach liquor in recovery furnace. The minimum cost function comprises of costs due to wash equipment (P_w), maintenance and repair (P_M), Power due to drum rotation, back shower pump vacuum pump, ($P_o * C_{13}$), for repulper-shredder ($P_o * C_5$), liquor spray ($P_o * C_6$), for screw conveyor the last BSW ($P_o * C_4$), evaporation ($P_E * C_E$), steam for hot wash water ($P_A * C_A$), steam generated due to heat value of BLS ($P_E * C_L$), condensate saving ($P_s * C_s$), bleach chemical consumption due to carry over solids ($P_{NB} * C_{NB}$), and labor cost (C_{LW}), cost of effluent treatment ($P_{Eff} * C_{Eff}$), cost due to soda loss ($P_{sl} * C_{sl}$), cost due to total solid loss ($P_{tsl} * C_{tsl}$). The objective function can be written as follows:

$$\text{Min } (C_T) = (P_w + P_m) * N + P_E * (C_E + C_A + C_L) + P_s * C_s + P_{NB} * C_{NB} + (C_{13} * N + C_5 * (N-1) + C_6 * N + C_4) * P_o + C_{LW} + P_{Eff} * C_{Eff} + P_{sl} * C_{sl} + P_{tsl} * C_{tsl}.$$

Where C_{13} = power consumption due to drum rotation (C_1) + back shower pump (C_2) + vacuum pump (C_3).

The problem envisaged above is the state of the art nature. Not much attempt has been made so far in India. Limited models are available in advanced countries like, USA, Canada and Scandinavia. The model so developed in this investigation can also be applied to other industries like, sugar industry. Thus the problem is of industrial and national importance.

CHAPTER 2

MATHEMATICAL MODELLING FOR WASHING

2.0 INTRODUCTION

Brown stock washing (BSW) is the key operation in a pulp mill controlling the cleanliness of pulp coming from digester with least carryover of dissolved solids to bleach plant on one hand and separating the maximum black liquor at as high a concentration as possible on the other. A carryover of black liquor solids with the washed pulp leaving for bleaching and paper making is a source of BOD, COD and other toxic pollutants harmful to the environment and involve huge expenditure for subsequent processing. Therefore the washing process needs optimization with respect to equipment, operating cost and environmental factors. Development of mathematical modeling is an imperative necessity to fulfil the above objective. For the above purpose, optimization of BSW is needed. Chap-1 depicts the development of objective function for multistage BSW. In the above objective function terms 1-8 are pertinent to the design and operation of BSW system.

The equipment cost of washing system in this present investigation is a function of number of washers (N) and surface area of a single washer. It is an usual practice in industry to keep the size of each washers same, primarily for easy replacement purposes and also the difference of area requirements for a particular capacity in each stage are not very significant. The area of each washer in turn depends upon fundamental parameters related to thermodynamics and fluid mechanics involved in cake such as permeability, porosity, density of fiber etc., external variables e.g. pressure drop, consistency, fractional submergence, and $\mu_{pm}(N)$, and viscosity of liquor. The total cost of the washing system thus can be estimated accordingly. Power consumption terms can

be calculated through appropriate equations relating to thermodynamics ,fluid mechanics and material balance equations for brown stock washer. The available equations developed earlier(7) after suitable modification are needed for the calculations.

To estimate the various cost items, separate models for each case has to be developed which need detailed understanding of the process. Table-2.1 reports regarding the ranges for the design and operational parameters for BSW. Therefore there is a need to have a fresh look about the static/steady state modeling of BSW system. In the following paragraphs, these are discussed.

Table-2.1 Normal range of different parameters

Parameter	Unit	Value
Inlet vat consistency	%	1-2
Outlet vat consistency	%	10-16
Cake thickness	m	0.025-0.040
Dilution factor	kg/kg	1-5
Fractional submergence of drum	-	0.25-0.45
Liquor speed in cake pores	m/s	0.003-0.006
Pressure drop across the cake	Pascal	20000-50000
Pulp temperature	⁰ C	60-90
Rpm	-	1-4

2.1 STEADY STATE MODELS RELATED TO WASHING EQUIPMENT

2.1.1 Models for Estimation of the Area of Drum

The estimation of the area of the drum can be modeled using material balance equation for differential length $l(z)$ of cake thickness and considering that laminar flow predominates during formation of mats on the washer. Using the combined equations due to Kozeny and Darcy for black liquor flow through porous bed of mat and neglecting filtration resistance of the mesh on the drum one can proceed as follows(92).

$$dV/dt = V_f = (K A \Delta P) / (\eta l(z)) \quad (2.1)$$

The above filtrate flow rate (black liquor) is a function of many parameters such as angle of submergence, radius of drum, pressure drop, rpm and properties of filtrate, slurry and cake. For a constant pulp suspension it depends upon radius of drum, rpm and angle of submergence.

Making a material balance between solids in the pulp slurry filtered and the solids in the cake (mats of fiber) and solute adsorbed in the cake for the same area A and any arbitrary thickness of the pulp mat $l(z)$, in any location of cake formation zone of the filter is given by,

$$(1 - \epsilon_t) A l(z) \rho_f + (1 - \epsilon_t) A l(z) \rho_f \{ABC / (1 + BC)\} = (V + \epsilon_t A l(z)) \rho X_i + (1 - \epsilon_t) A l(z) \rho_f \{ABC / (1 + BC)\} \quad (2.2)$$

During cake formation, the adsorption of solutes (sodium based and lignin) along with pulp fiber can be neglected as the values of constants of Langmuir adsorption isotherm constants are small. Hence for macroscopic steady state balance the following equation holds.

$$(1 - \epsilon_t) A l(z) \rho_f = (V + \epsilon_t A l(z)) \rho X_i$$

This, on rearrangement, one can get

$$l(z) = \rho X_i V / [A \{(1 - \epsilon_t) \rho_f - \epsilon_t \rho X_i\}]$$

If $l(z)$ is eliminated from Eq.(2.1) and (2.4), one can get the following equation

$$V(dV/dt) = [K \Delta P A^2 \{(1 - \epsilon_t) \rho_f - \epsilon_t \rho X_i\}] / \eta \rho X_i$$

After integration, one can get the total volume of the filtrate collected through the formation zone as under

$$V=[AL\{(1-\varepsilon_t)\rho_f-\varepsilon_t\rho_{X_i}\}]/\rho_{X_i} \quad (2.6)$$

The volume of filtrate through cake formation zone can be written as follows

$$V_f=NAL\{(1-\varepsilon_t)\rho_f-\varepsilon_t\rho_{X_i}\}/\rho_{X_i} \quad (2.7)$$

$$V_f=A[2K\Delta P\{(1-\varepsilon_t)\rho_f-\varepsilon_t\rho_{X_i}\}\psi N/\eta\rho_{X_i}]^{1/2} \quad (2.8)$$

$$=A[2K\Delta P\{(1-\varepsilon_t)(1-C_{yi})-\varepsilon_t\rho_{C_{yi}}\}\psi N/\eta\rho_{X_i}]^{1/2} \quad (2.9)$$

Eliminating V from Eqs.2.1 and 2.4, the following equation results

$$l(z)(dl/dt)=K\Delta P\rho_{X_i}/[\eta\{(1-\varepsilon_t)\rho_f-\varepsilon_t\rho_{X_i}\}] \quad (2.10)$$

which on integration between $t=0$ to $t=\psi/N$, assuming ΔP as constant, where ψ/N corresponds to cake formation time, following expression can be developed

$$L=[2K\Delta P\rho_{X_i}\psi/\eta N\{(1-\varepsilon_t)\rho_f-\varepsilon_t\rho_{X_i}\}]^{1/2} \quad (2.11)$$

$$=[2K\Delta P\rho_{C_{yi}}\psi/\eta N\{(1-\varepsilon_t)(1-C_{yi})-\varepsilon_t\rho_{C_{yi}}\}]^{1/2} \quad (2.12)$$

$$=[2K\Delta P\rho_{C_{yi}}\psi/\eta N(1-\varepsilon_t)(1-mC_{yi})\rho_f]^{1/2} \quad (2.13)$$

For estimation of the area, the other process parameters as indicated above can be summarized in the Table-2.2.

The Eqs.1-9 depicted in the Table-2.2 are required for simulation using data from the work of Perron and Labeau(78). The data is depicted in Table-2.3. The fixed charges related to equipment cost can only be found provided the cost of equipment Rs/m² is known. The details of the cost estimation is discussed in Chap-6.

Table - 2.2 Important parameters required to estimate the area of the washer

S. N.	Parameters	Formula
1.	C_{sl}	$C_{sl} = \rho C_{yi} / (1 - C_{yi})$
2.	m	$m = [\varepsilon_t \rho + (1 - \varepsilon_t) \rho_f] / [(1 - \varepsilon_t) \rho_f]$
3.	m_p	$m_p = C_{sl} \rho / [\rho - (m - 1) C_{sl}]$
4.	ε_t	$\varepsilon_t = (1 - C_y) \rho_f / [\rho C_y + \rho_f (1 - C_y)]$
5.	f	$f = (\theta / 2\pi) = (1/\pi) \cos^{-1} [(R_0'' + R - N_2) / R]$ where $\theta = 2 \cos^{-1} [(R_0'' + R - N_2) / R]$
6.	K	$K = \varepsilon_t^3 / [k_1 S_0^2 (1 - \varepsilon_t)^2]$
7.	FPR	$FPR = (1 - \varepsilon_t) N A L \rho_f = A [2(\Delta P)^{1-s} \rho C_{yi} \psi N / \eta \alpha_0 (1 - C_{yi})]^{1/2}$
8.	A	$A = FPR / (1 - \varepsilon_t) * N * L * \rho_f$
9.	A	$A = (V/t_c) [C \alpha_0 \mu t_c / 2(-\Delta p)^{1-s} g_c f]^{1/2}$

Table-2.3 Data of Perron and Lebeau(78)

Parameter	Unit	Value	Parameter	Unit	Value
A	m^2	0.430×10^2	ε_t	-	0.940
K	m^2	$.6905 - 0.789 \times 10^{-11}$	η	kg/s	0.620×10^{-3}
N	1/s	0.250×10^{-1}	θ	Radian	0.214×10^1
ΔP	Pascal	0.200×10^5	ρ	Kg/m^3	0.100×10^4
R	m	0.175×10^1	ρ_f	Kg/m^3	0.156×10^4
S_0	m^2/m^3	0.156×10^7	ψ	-	0.340
x_i	kg/kg	0.119×10^{-1}	ε_d	-	0.50
L	m	2.957×10^{-2}			
V_w	m^3/s	2.500×10^2			
C_i	Kg/m^3	1.105×10^1			

2.1.2 Model for Estimating Total Power Consumption(P) for multi-stage BSW

From the detailed plant study of BSW system it is found that this term includes the power consumption for spray water/ recycled liquor in different stages, drum rotation, for repulper - shredder, screw conveyer and vacuum pumps(if required)

Total power consumption for a BSW system of N stages can be expressed as follows:

$$P=\{P_1+P_2(DF)+P_3+P_6\} *N+P_4+P_5*(N-1) \quad (2.14)$$

a. Power required for pump of liquor from seal tank(P₂)

Using Bernouli's equation Eq.(2.16) the power consumption for pumping the black liquor from seal tank to wash the pulp of previous stage can be calculated in the usual way assuming $V_1=V_2$ at the inlet and outlet conditions of drop leg pipe, and also the filtrate is incompressible($\rho_2=\rho_1 =\rho$)

$$Z_1+P_1/\rho_1+V_1^2/2g= Z_2+P_2/\rho_2+V_2^2/2g \quad (2.15)$$

One can get, $\Delta P=\rho(Z_2-Z_1)$

Total head developed $\Delta H(\text{meter})= \Delta P/\rho$

Power consumption for liquor spray can be calculated by the following equation

$$P_2(\text{kW})=Q \rho g H/1000\eta; Q\rho=(DF+L_p)FPR \quad (2.16)$$

Where Q =flow of liquor, m^3/s , ρ =density of liquor, kg/m^3 , H = total head developed, η =overall efficiency of pump. L_p =liquor with the pulp, kg/kg

Material balance of brown stock washing gives the liquor flow rate at different

dilution factors per tonne of pulp. It is known that liquor flow increases by increasing the dilution factor. If one knows the plant capacity or fiber production rate, and drop leg height and the level of immersion of the pipe in seal tank as recommended by Shackford (97) and Perkins (76), the power consumption can be calculated.

b. Power required for drum rotation (P₃)

Referring Table-2.1 BSW rotates at a specific rpm. If rpm is known the power for this can be calculated

$$P_3(\text{hp}) = T \cdot N / 63000 \quad (2)$$

$$P_3(\text{kW}) = 0.75 \cdot T \cdot N / 63000, \quad \text{where } T = \text{torque lb-ft, } N = \text{rpm, } 1/\text{s}$$

Using industry data for all the variables and motor efficiency one can estimate the power consumption for drum rotation is 11.25 kW for each drum in a multi-stage washer.

c. Power required for screw conveyer at the last BSW(P₄)

Pulp sheet of high density is to be shredded up by using screw conveyer at the last BSW to prevent undue difficulties in removing it from the storage tank. The stock is diluted in the repulper. Power is thus estimated by the following equation:

$$P_4(\text{W}) = C \cdot L \cdot W \cdot F / 33000 \quad (2)$$

where C=capacity, ft³/min, L=length, ft, W=weight of material, lb/ft³, F= material factor.

d. Power required for repulper -shredder(P₅)

Referring from Fig.2.0 it is a practice in industry to repulp the discharge mat with recirculated black liquor from previous stage which necessitates shredder operation to bring down to 1-1 consistency and is led to the vat of subsequent stage. The number of repulper and shredder is usually one less than the number of washers. From a standard mill practice it is observed that power on the order of 7.5 kW is required. Thus for N repulper shredder 7.5×(N-1) kW is required. Where N is the number of washers.

e. Power required for back shower pump(P₆)

For cleaning the decker/washer, water is required which is termed as back shower. This involves pumping of back-water. Further it is noticed from paper mill the value ranges from 5.25 to 5.63kW, using the higher values one can get

Power required for N back shower pumps = $N \times 5.63 \text{ kW}$

f. Power requirement of vacuum pump(P_1)

It is well known that vacuum pump operates between suction pressure below atmospheric and discharges against atmospheric. In paper industry brown stock washer, this is required if dropleg is not sufficient(107). Most of the Indian stable BSW do not suffer from this limitation for the necessity of a vacuum pump to create required vacuum. In poorly designed mills however this pump is needed to create sufficient vacuum. Power consumption for a vacuum pump is given by the following equations for a single stage system.

$$P_1 = G \cdot W_{ad} / 3600 \cdot 1000 \quad (2.19)$$

$$W_{ad} = [\gamma / (\gamma - 1)] p_1 v_1 [(p_2 / p_1)^{(\gamma-1)/\gamma} - 1] = [\gamma / (\gamma - 1)] RT_1 [(p_2 / p_1)^{(\gamma-1)/\gamma} - 1] \quad (2.20)$$

where $R = 488 \text{ J/kg.K}$, $\gamma = C_p / C_v = 1.4$ for air (adiabatic exponent)

G can be calculated from density and volume of air displacement per hour, which in turn depends upon the values of fraction submergence of drum, fraction of drum area available for air suction(k_a), viscosity of filtrate(μ), viscosity of air at room temperature(μ_a), specific resistance of cake(r) and specific air suction cake resistance(r_a).

In the present investigation, $r/r_a = 0.6$

Volume of air displaced per unit time/ weight of cake per unit time

$$= k_a \mu r / k_f \mu_a 2 r_a C \quad (2.21)$$

$C =$ mass of dry cake deposited per unit volume of filtrate $= 19.15 \text{ kg/m}^3$

$$\text{Volume of air displaced per unit time}(V_2) = (k_a / k_f) (\mu / \mu_a) (r / r_a) (1 / 2C) \text{FPR} \quad (2.22)$$

$$\text{and } V_1 = V_2 (P_2 / P_1) \quad (2.23)$$

2.2 STEADY STATE MATHEMATICAL MODELLING

Material balance for N stage BSW is required to get many output parameters such as solids percentage and feed flow rate to the evaporator as a function of pulp production rate with varying

vat consistency, blow pit consistency and dissolved solids in the vat liquor. In some cases for existing plant some input parameters (flow rate and concentration) in recycle stream may not be known. The final washed pulp consistency can also be varied with varying input parameters. The above parametric influences for a fixed mill capacity (pulp production rate) on the impact on bleaching and evaporator plant can be assessed if material balance calculations are performed. It is not out of place to mention that the impact on evaporator will be transferred to recovery plant in greater magnitude; further impact on bleach plant will be amplified in terms of higher steam and chemical consumption and more dangerously pollution load generation affecting ecology and environment.

The efficiency and efficacy of brown stock washer are quantified by many ways such as Displacement ratio (DR), Solid reduction ratio (SRR) and equivalent displacement ratio (EDR) and finally the Norden and modified Norden efficiency factors. Displacement ratio and solid reduction ratio concept developed by Perkins (77) are widely used as coefficient of the material transfer in the pulp mat. Shackford (97) advocated the use of DR for design. Tyagi (117) has shown that the difference between the values between DR and EDR are not significant. Therefore, in this present investigation the procedure of Shackford (97) and Perkins (77) are followed. The experimental values of DR for three stages are extrapolated and interpolated for smaller and larger number of stages. This approximation does not introduce any serious error and is permitted in engineering estimation.

Overall material balance requires the samples of the blow liquor, liquor to the evaporators, and liquor in the pulp leaving the system. From these data a liquid and soluble solids balance can be made, which can give the performance of the entire system in terms of the percent solids removed for a given amount of dilution water entering the system. This method is valuable for a complete

system. To determine the amount of washing accomplished by each step in the washing process the solid reduction ratio method is used, which is discussed in the following paragraph.

2.2.1 Mathematical modeling for computation of solid reduction ratio for any number of stages in a multistage washer

The term solid reduction ratio is introduced by Mappus(77)and later reproduced by J.A. Smith, Jr.(103). This concept does illustrate that a washing system is basically a fractionating device and that the solids reduction in any stage of the system is a function of the solids content of the entering liquor.

This procedure relates the solids content of the liquor in the pulp leaving the final stage of a washing system to the solids content of the liquor in the pulp as blown. For a washing system with m stages:

$$R_1=S_1/S_b; R_2=S_2/S_1; \dots\dots\dots; R_m=S_m/S_{m-1} \tag{2.24}$$

The overall performance of a multistage washer system would be the product of all the solids reduction ratios

$$(R_1 \times R_2 \times \dots \times R_m) = S_m/S_b \tag{2.25}$$

It is assumed that all vat and sheet consistencies are the same in derivation of the R factors but exact values from field data may be substituted when known. Perfect mixing in the vat is assumed.

The foundation of this concept is the fact that there is a relationship between the displacement ratio and the dilution factor. Considering a system with m stages,

$$S_a = R_a S_{a-1} \tag{2.26}$$

The R terms are simple ratios, which can be calculated as follows

$$R_b = W_b/W_p, R_v = W_p/W_v, R_s = W_p/W_{ts}, R_e = W_p/W_e, R_g = W_s/W_{ts} = R_s(DR) \tag{2.27}$$

Product of R terms is

$$\Pi R_{(1 \rightarrow m)} = R_1 \times R_2 \times \dots \times R_m \tag{2.28}$$

$$W_{ts}S_{a(m-1)} + W_p S_m = W_{ts} S_s + W_p S_{m-1} \quad (2.2)$$

$$S_{s(m-1)} = (W_p / W_{ts})(S_{m-1} - S_m) = R_s(S_{m-1} - S_m) \quad (2.3)$$

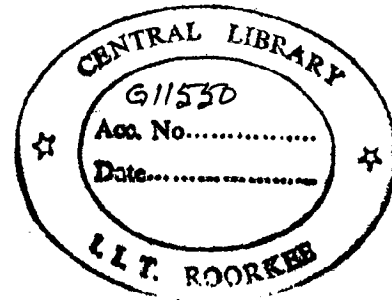
Solids in vat are given by

$$S_v = [W_p S_{(m-1)} + W_v S_{s(m-1)}] / W_v = (W_p / W_v)(S_{m-1}) + [(W_v - W_p) / W_v](S_{s(m-1)}) = R_v S_{(m-1)} + (1 - R_v)[R_s(S_{m-1} - S_m)] \quad (2.3)$$

$$R_{gm} = R_s (S_v - S_m) / (S_v - S_s) = R_s (S_v - S_m) / (S_v) \quad (2.3)$$

Solids from final stage can be expressed as

$$\begin{aligned} S_m &= [1 - (R_{gm} / R_s)] \cdot S_v \\ &= [1 - (R_{gm} / R_s)] [R_v S_{m-1} + (1 - R_v) \{R_s(S_{m-1} - S_m)\}] \\ &= [1 - (R_{gm} / R_s)] [R_v + (1 - R_v) R_s] S_{m-1} / [1 + (1 - (R_{gm} / R_s))(1 - R_v) R_s] \end{aligned} \quad (2.3)$$



$$S_m = R_m \cdot S_{m-1}$$

Solid reduction ratio from final stage is given by

$$R_m = (1 - R_{gm} / R_s) [R_v + (1 - R_v) R_s] / (1 + R_s(1 - R_{gm} / R_s)(1 - R_v)) \quad (2.3)$$

Solid reduction ratio of middle stage is given as

$$\begin{aligned} R_a &= (1 - R_{ga} / R_s) [R_v + (1 - R_v) R_s] / ((1 + R_s(1 - R_{ga} / R_s)(1 - R_v))(\prod R_{a+1 \rightarrow m}) \\ &\quad - R_{ga} (1 - \prod R_{a+1 \rightarrow m})) \end{aligned} \quad (2.3)$$

Solid reduction ratio from first stage can be calculated as

$$\begin{aligned} R_1 &= (1 - R_{g1} / R_s) [R_v R_b + (1 - R_b R_v) R_c R_b] / ((1 + R_c(1 - R_{g1} / R_s) \\ &\quad (1 - R_b R_v)(\prod R_{2 \rightarrow m}) - R_{g1} (1 - \prod R_{2 \rightarrow m})) \end{aligned} \quad (2.3)$$

$$S_m = R_1 * R_2 * \dots * R_m * S_b = (\prod R_{a \rightarrow m}) S_b \quad (2.3)$$

Now, one can calculate the following

- Total solids out with sheet, kg/tonne pulp = $TS = S_m * W_p * FPR$
- Total soda loss as Na_2SO_4 , kg/tonne pulp = $TSL = TS / 1.74$
- Percentage solid to evaporator = $S_e = (W_b S_b - W_p S_m) / (W_b + D)$

The formula derived by Perkins(77) can be used for the estimation of R_n for any intermediate stage of a multistage system and also the improvement of additional stage may be readily estimated and the stepwise calculation can be simplified.

2.2.2 Steady State Material Balance for Multiple Stage Counter Current(four) washers

Fig.2.0 indicate a four stage BSW problem. A general material balance equation for the same can be written as follows.

First washer mass balance:

Liquor:

$$L_C + L_B + L_G = L_F + L_H$$

$$L_F = L_D + L_E$$

$$L_D = L_B + L_A$$

$$L_F = L_C + L_B$$

Solids:

$$L_C X_C + L_B X_B + L_G X_B = L_F X_F + L_H X_H$$

$$L_F X_F = L_D X_D + L_E X_D, L_D X_D = L_B X_B + L_A X_A$$

$$L_F X_F = L_C X_C + L_B X_B$$

Second Washer mass balance:

Liquor:

$$L_I + L_H + L_L = L_K + L_M, L_K = L_G + L_I$$

$$L_{KI} = L_I + L_H$$

Solids:

$$L_I X_I + L_H X_H + L_L X_L = L_K X_K + L_M X_M$$

$$L_K X_K = L_G X_G + L_I X_I$$

$$L_{KI} X_{KI} = L_I X_I + L_H X_H$$

Temperature rise= $\Delta t=T_2-T_1$

Wash flow, kg liquor/kg pulp = $W_{ts}=W_p+DF$

Wash water applied to the sheet,kg liquor/kg pulp= $W_p=(1-C_{yd})/C_{yd}$

2.3. RESULTS AND DISCUSSIONS

A logic diagram for BSW design for calculation purpose is shown below:

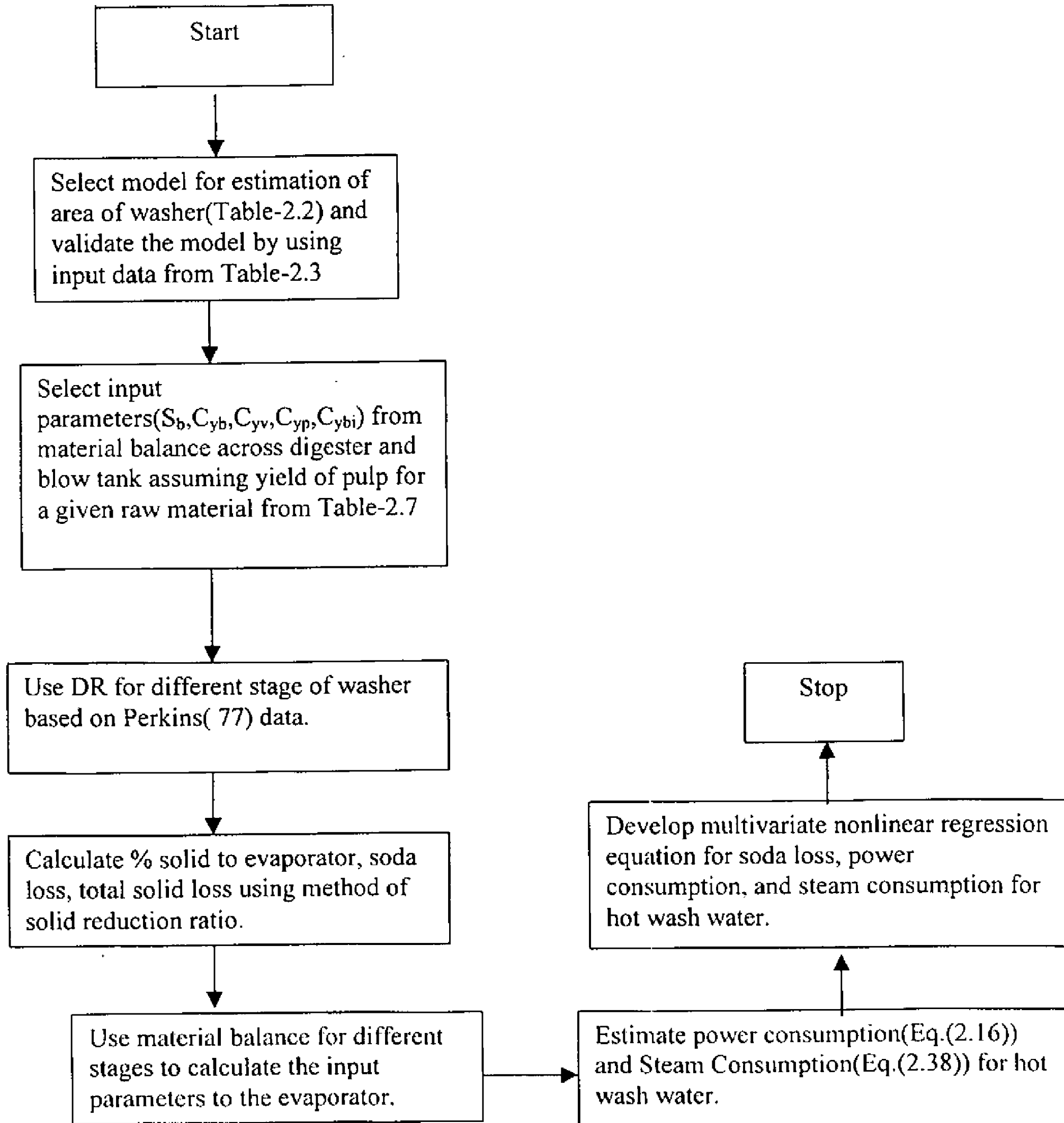


Table-2.4 Blow liquor % solids, % solids to evaporator, consistency of pulp at DF 3.5

Pulp yield,%	%Blow tank liquor solids	% Solids to evaporator	Solids from blow tank t/t pulp	Liquor from blow tank t/t	Consistency to blow tank, %
50	26.00	17.80	1.948	7.44	11.83
47.68	26.65	18.1	2.089	7.84	11.31
45	27.40	19.15	2.27	8.38	10.63
40	29.99	21.51	2.834	9.708	9.2

Table-2.5 Blow liquor % solids, % solids to evaporator, consistency of pulp at DF 2.5

Pulp yield,%	%Blow tank liquor solids	% Solids to evaporator	Solids from blow tank t/t pulp	Liquor from blow tank t/t	Consistency to blow tank, %
50	26.56	19.59	1.948	7.44	11.83
47.68	26.65	20.20	2.089	7.84	11.31
45	27.87	20.90	2.27	8.38	10.63
40	30.48	23.21	2.834	9.708	9.2

In fact these calculations are made with combined digester output, blow tank and BSW systems. The methodology for different pulp yield between 40-50 are extended for both DF 2.5 and 3.5. The parameters are % blow liquor solids, % solids to evaporator, black liquor solids per tonne of pulp and consistency of pulp as a function of pulp yield and DF. These are shown in Tables-2.4 and 2.5. The values of the parameters are also checked if one does not consider relief vapors and flash steam generated in material balance calculations. It is clear from the Table-2.4 and 2.5 that there is

no effect on liquor from blow tank, t/t, solids from blow tank, t/t and consistency to blow tank. Only % liquor solids in blow tank and solid to evaporator will change.

The above data are important as these data are reliable, applicable to Bamboo or hardwood bleached liquors for further simulation in this investigation. Therefore, these data have been employed as a basis for further calculations.

It is interesting to note that the Table-2.4&2.5 that with the decrease of pulp yield from 50% to 40% the blow tank liquor solids and % solid to evaporator increased. It is applicable to both the DF of 3.0 and 3.5. With the decrease of DF as expected again there is an increase of both the parameters.

The yield value have been chosen between 40-50% because both good and bad quality bamboo or hardwood ranges in between. The high values of % solids to evaporator are not surprising. For normal yield of 47.5% of pulp, with indirect steaming and higher number of stages(5-6) the solids to evaporator may be of the order of 22-22.9%(64).

2.3.1 Area of drum

Validity of model for area estimation by using the data of Perron and Lebeau(78)

For validity of equations, data of a four stage industrial washing plant, reported by Perron and Lebeau(78) is used. This data is given in Table-2.3. The value of cake thickness and area predicted by Perron and Lebeau(78) is examined with the value of cake thickness and area obtained from present equations. There is good agreement observed between these two sets of data with an error of only 2.6%. These are allowed for any engineering design calculations.

Eq.(8) of Table -2.2 is used for this purpose. This is further cross-checked with the Eq.(9). Both are matching each other. This equation is also used to show the effect of FPR and cake thickness on area of drum. The results obtained are plotted in Figs. 2.12 to 2.15. Results are given in the following Table-2.6

Table-2.6 Area and thickness of BSW

Parameter	Unit	Value
Thickness	m	.02712
Area	m ²	41.817
Area	m ² /tonne pulp	14.817

In the present investigation the above models given in Sections 2.2.1 and 2.2.2 are made in the form of algorithm given in APPENDIX-I and subjected to computer program with C++ for detailed calculations. In the absence of Industry data the data from literature(64) is used for simulation of the steady state model of material balance alongwith solid reduction ratio calculation. The values of various parameters required for the above calculations are shown in Table-2.7

Table-2.7 Input Parameters

S _b	26.65
C _{yb}	11.31
C _{yv}	1.25
C _{yp}	16.0
C _{ybi}	3.0

These data are standard data in North-American mills. These are again cross-checked with classical material balance calculations for DF 3.5 made by Macdonald(64).

The results are given in APPENDIX-VI Table-1. From Table, it is observed that increase in dilution factor has resulted in cleaner pulp though the concentration of solids in black liquor going to evaporator has reduced from 24.41% to 16.22% at DF equal to 0 to 5 for three washers. The

values of soda loss, kg/t and total solid loss as a function of DF and N are also shown there in. / expected there are decreased with increased both DF and N.

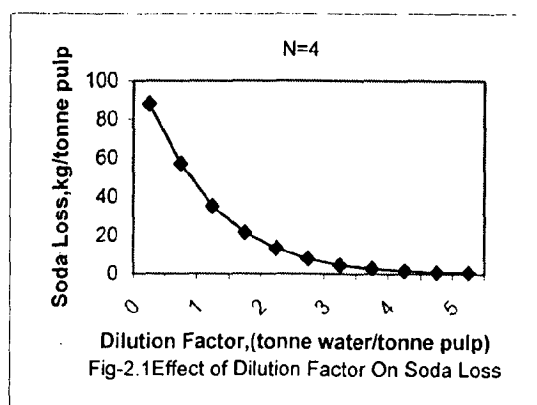
Material balance given in Section 2.2.2 based on computer program in C++ gives the values of liquor and solid in each stream of Fig. 2.0. Amount of liquor from seal tank to spray, liquor to evaporator for various dilution factors are given in the Table-2 of APPENDIX-VI

Eq.(2.38) is used to calculate steam consumption for hot wash water. Power consumption for liquor is calculated by Eq.(2.16). A representative set of computed results is given in APPENDIX VI Table-2.

The data generated are plotted in graphs for better interpretations for four number of washers. Similar data have also been generated for three and two stage also. In the following paragraphs the parametric effects are shown for four stage washers. These are described below:

2.3.2 Effect of Dilution Factor on Soda Loss

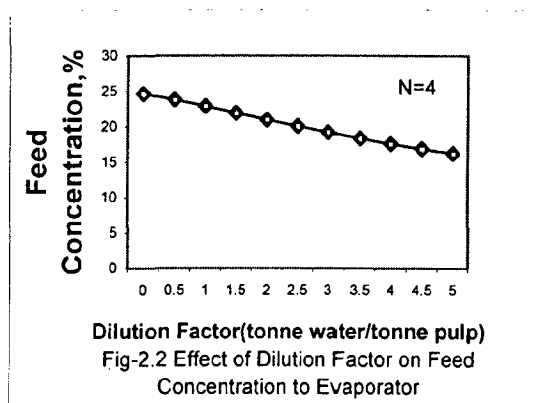
Effect of dilution factor on soda loss as sodium sulphate has been shown in Fig. 2.1 for the last stage of a four stage washer. It is observed that with the increase of dilution factor from 0.0 to 5.0 soda loss decreases. The trend of the curve is strongly nonlinear resembling exponential in nature.



On closer scrutiny of the results, it is found that there is insignificant soda loss for dilution factor above 4.0. For 3.5 dilution factor which is the usual value of DF in three stage washers in pulp and

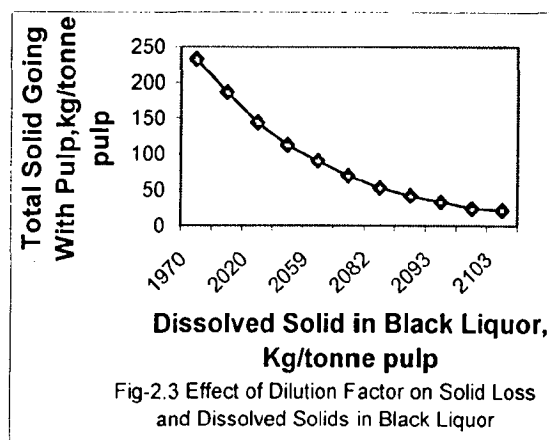
paper industry the value lies between 8-3 kg/ t of pulp. The value is quite close to the values reported by Sepall et.al.(96) and Mc-Donald(64).

Fig.2.2 shows the effect of dilution factor on feed concentration to evaporator for four washers. With the increase of dilution factor, solids of black liquor going to evaporator increases and amount of liquor to evaporator also increases. As a result of this with the increase in dilution factor



feed concentration decreases very rapidly in linear manner. Change in DF 2.5 to 4 shows the reduction of 2.46% of black liquor solids to evaporator.

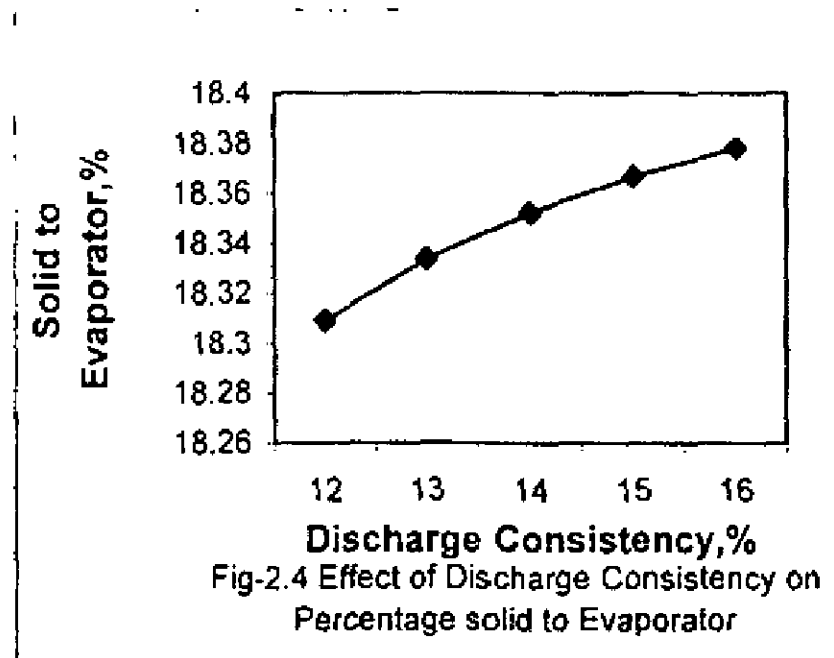
Fig. 2.3 has been drawn to show the effect of dissolved solid in black liquor on total solid loss, kg/tonne pulp. With the increase in dilution factor solid loss decreased(Fig. 2.1). On the other hand increase in dilution factor results in increased dissolved solid in black liquor, kg/tonne pulp. Hence



with the increase in dissolved solids in black liquor, total solid loss is reduced. Increase in DF 2 to 4.0 the total solid loss is reduced from 14.06 to 3.56kg/t and black liquor solids to evaporator increases from 2.069 to 2.093 t/t.

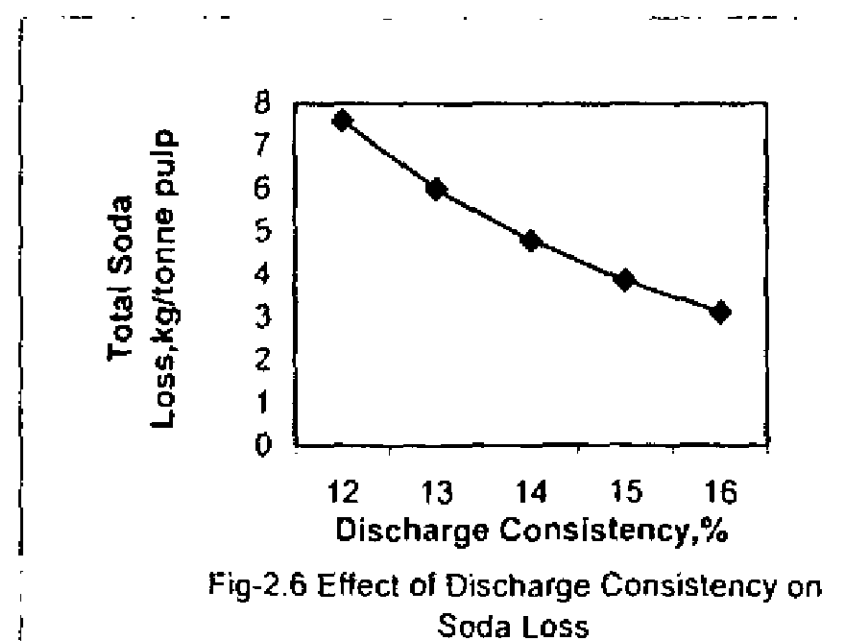
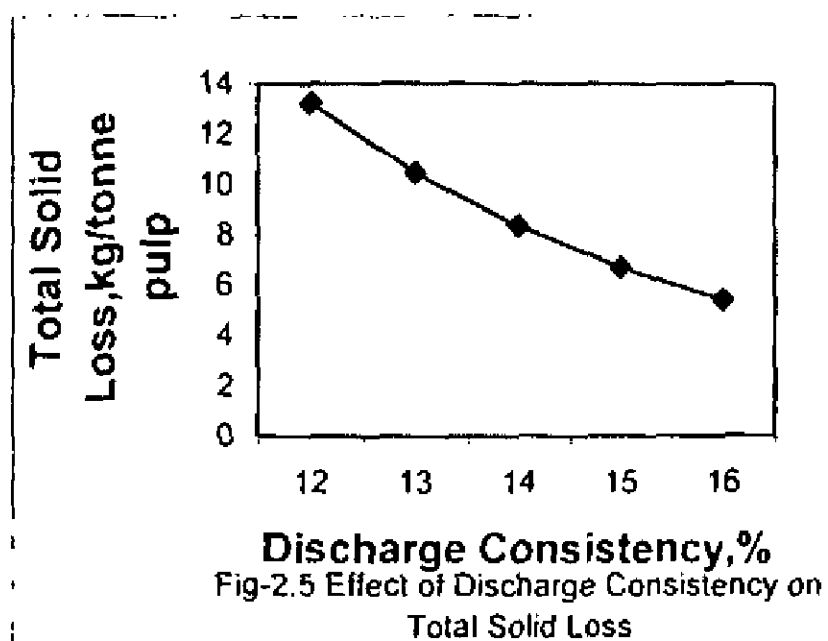
2.3.3 Effect of Discharge Consistency

Figs. 2.4 shows the effect of discharge consistency on solid percentage to evaporator. With the



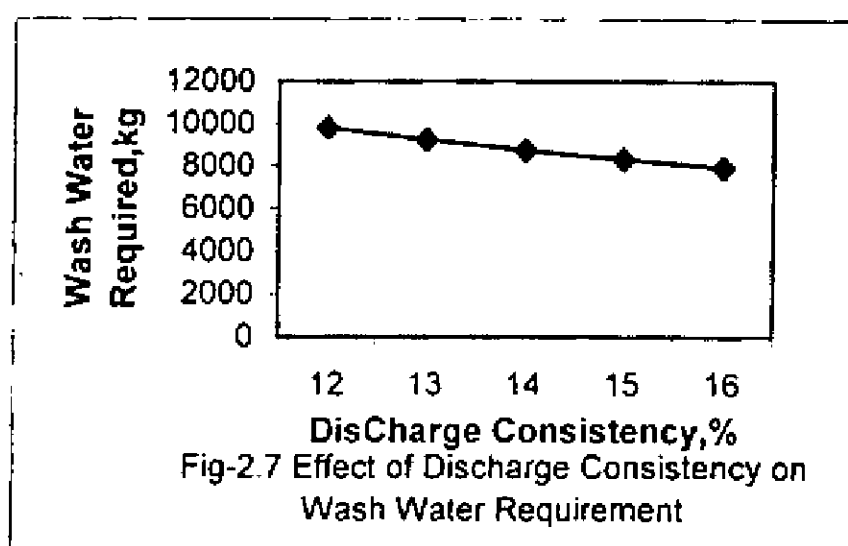
increase in discharge consistency results in slight increased of percentage solids. The trend of the curve is nonlinear in nature. The increase in solid percentage to evaporator will be of the order of 18.3092% to 18.3781% when discharge consistency is increased from 12% to 16%.

Figs. 2.5 and 2.6 are drawn to show the effect of discharge consistency on total solid loss and soda



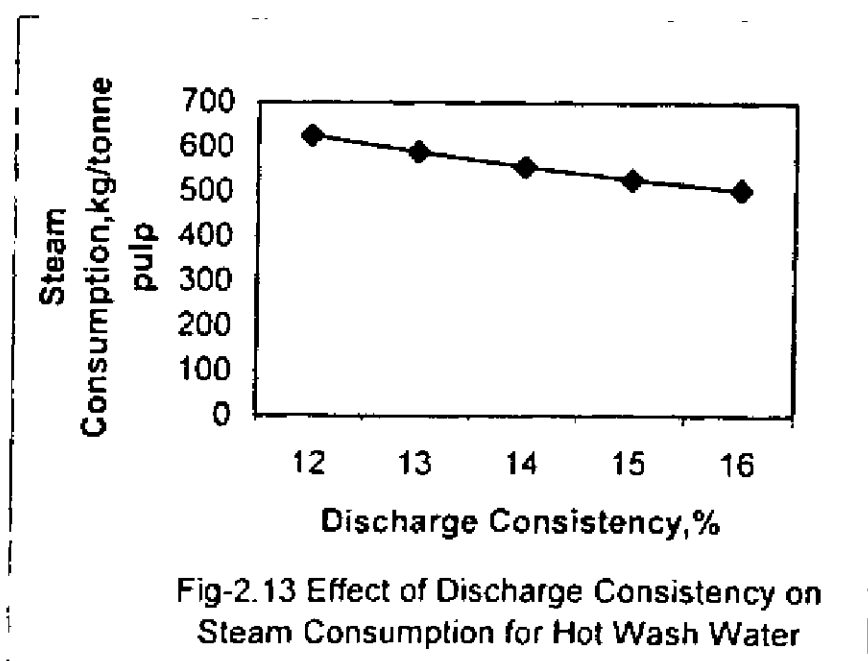
loss, kg/tonne pulp. With the increase of discharge consistency nonlinear decreasing trend of total solid loss and soda loss are observed. The reduction in total solid loss will be from 13.23 to 5.43 kg/t when discharge consistency is increased from 12% to 16%. The decrease in total soda loss will be approximately 7.60 to 3.12 kg/t when percentage of discharge consistency is increased from 12 to 16.

From Fig. 2.7 it is evident that if the discharge consistency increases, wash water requirement decreases linearly. Although discharge consistency has minor effect on wash water requirement but has a significant influence on total cost of washing in the plant. Approximately 19% reduction



is observed in wash water requirement when discharge consistency changes from 12 to 16 %.

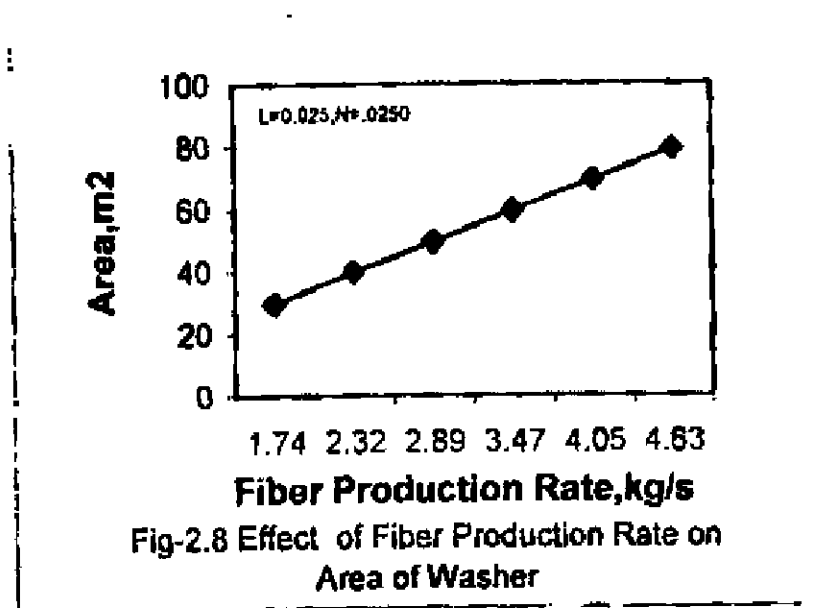
It is evident from Fig. 2.13 that as we go on increasing discharge consistency, steam consumption for hot wash water will be decreased. With the increase in discharge consistency from 12 to 16 % there is a decrease in steam consumption from 626 to 506 kg/tonne pulp. If considered annually it



has a great influence on total cost of washing.

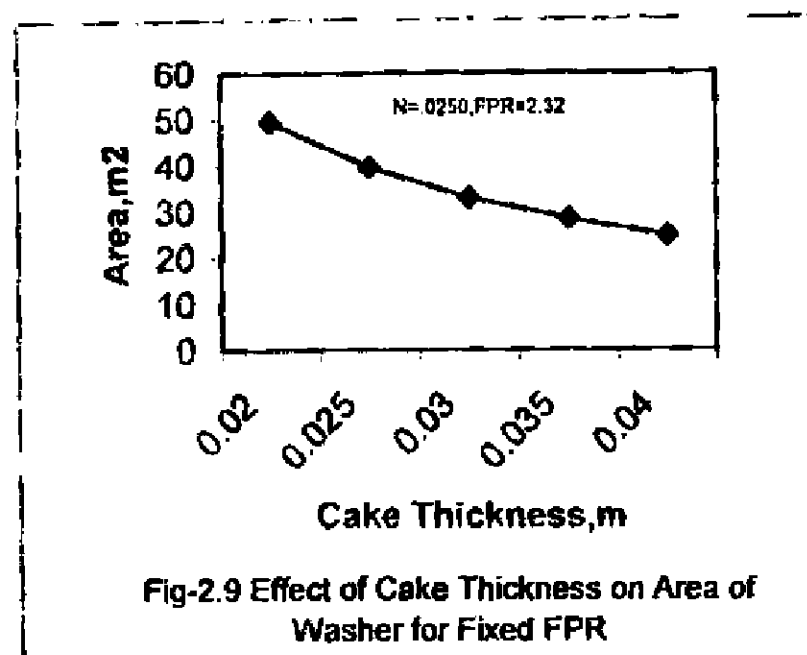
2.3.4 Effect of FPR and Cake Thickness on the Area of Washer

Fig. 2.8 shows the effect of fiber production rate on area of washer. With the increase in fiber production rate results linearly increased area of washer at a fixed cake thickness values. This figure is drawn using the results obtained from Eq.(8) of Table-2.2. If FPR is increased from 1.74



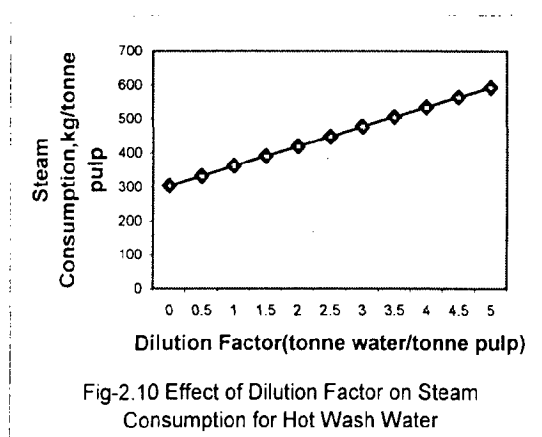
to 4.63 kg/s then area is increased from 29.74 to 79.14 m².

Fig.2.9 shows the effect of cake thickness on area of washer at a fixed fiber production rate. With the increase of cake thickness, area of washer will be decreased nonlinearly. A reduction in area from 49.5 to 24.78 m² is observed with the increase in cake thickness from .020 to .040m.



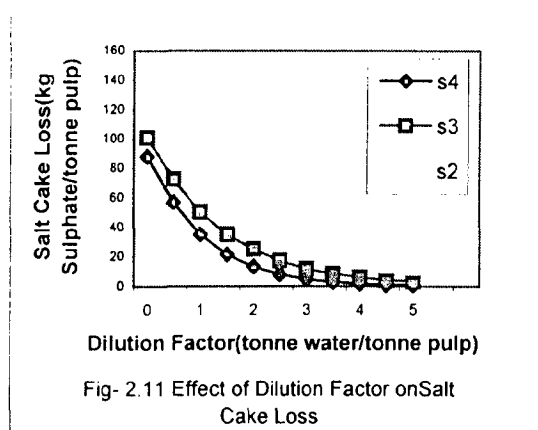
2.3.5 Influence of Dilution Factor on Steam Consumption for Hot Water

Fig.2.10 has been drawn to show the effect of dilution factor on steam consumption for hot wash water. Cost of hot wash water depends upon steam consumption. With the increase of dilution factor, steam consumption will be increased at a fixed temperature. It is evident from the figure that number of washers has no effect on hot wash water used. Hence it is a function of DF only. Steam consumption increases of the order 16.26% with the increase in DF from 2.5 to 4.



2.3.6 Combined Influence of Dilution Factor and Number of Stages on Soda Loss

Fig.2.11 shows the effect of dilution factor and number of washers on soda loss kg/tonne pulp in terms of sodium sulphate. It is evident from the figure that with the increase in dilution factor from 0 to 4 there is a rapid decrease in soda loss. The trend of the curve is exponential in nature

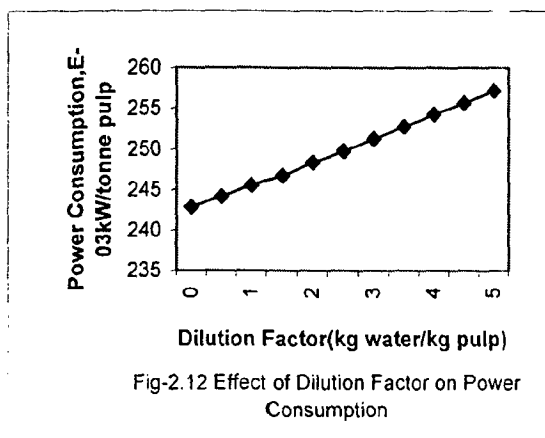


with strong non-linear characteristics. As expected the soda loss decreases if the number of stages

become higher. For DF equal to 2.5 the soda loss for two, three and four stage washer 40.24,17.43 and 8.08 kg/t respectively.

2.3.7 Effect of Dilution Factor on Power Consumption due to Wash Water Spray

This power consumption is due to wash water spray from the seal tank of the successive bod the preceding filter. This is a function of amount of the wash liquor(hence DF) for the respec body which is actually independent of fiber production rate. Therefore power consumption expressed as a function of dilution factor only.Fig.2.12 has been drawn to show the effect



dilution factor on power consumption, kW/tonne of pulp. The graph reflects that there is a dir linear relationship between them.

Regression Analysis:

The regression equations for soda loss, power consumption for liquor spray and stea consumption for hot wash water are obtained by using the data of Table-1 and 2 of APPENDI VI. These are as follows:

$$\text{Soda loss}=4.25(\text{DF}*\text{N})+6.593(\text{N}^2)-65.947(\text{N})+236.164-59.176(\text{DF})+5.602(\text{DF}^2), \text{ with } R^2=0.988 \quad (2.39)$$

$$\text{Power}=0.243+2.693\times 10^{-3}(\text{DF})+3.776\times 10^{-5}(\text{DF}^2), \text{ with } R^2=1 \quad (2.40)$$

$$\text{HWW}=303.67+57.844(\text{DF})-2.331\times 10^{-4}(\text{DF}^2), \text{ with } R^2=1 \quad (2.41)$$

2.4 CONCLUSIONS

Various algorithms have been developed for solid reduction ratio of Perkins(77) and material balance for multistage washers. These are subjected to computer program C++ and data are generated. Based on the data and the figures drawn the following conclusions can be drawn.

Soda loss, total solid loss and percentage solid to evaporator decrease with the increase in dilution factor. Soda loss and total solid loss decrease with the increase in number of stages at any given dilution factor. Steam consumption for hot wash water, power consumption due to liquor spray also increase with the increase in dilution factor . This is in close agreement with those obtained from the previous investigators. These effects will be subsequently used in optimization of BSW.

CHAPTER-3

MATHEMATICAL MODELING OF BLACK LIQUOR MEE

3.0 INTRODUCTION

It has already been indicated in Chap-1 that Indian mill consumes approximately 9.5 to 20 ton steam per tonnes of finished paper. This high energy consumption calls for reducing steam consumption thereby achieving gain in thermal efficiency by utilizing various plausible methodologies. Some of them are: use of multiple bodies in a set, the liquor flow sequence, use of LTV in place of steam flashing of condensate and product and so on. Three important parameters related to evaporator system design, optimization, modeling and simulation are steam consumption, steam economy and area requirements of the evaporator bodies, also called capacity.

As earlier stated, steam economy(SE) is defined as the kg of water evaporated per kg of steam consumed whereas capacity is the kg of water evaporated per square meter of heating surface.

The steam consumption, steam economy and area requirements for MEE vary with the various input weak black liquor and output product liquor concentration, temperature of steam and liquor, vacuum in the last body and the feed flow rate. These are also influenced by pressure and temperature distribution in each and individual bodies. These must be clearly identified before approaching for optimal design of MEE.

Unfortunately, the information in this regard is not available to the designer of MEE systems particularly, for black liquor concentration. Sufficient data are not available to find it. No standard method exists to accurately estimate these parameters. Hence there exists enough room to investigate the parametric influence on steam consumption and related issues.

Many correlations for physico-thermal/ physico-chemical properties of black liquor are reported in literature (37,43). In fact, all are not suitable for prediction for the property of the liquor, normally used by Indian mills because of its dependency on raw materials, pulping process conditions and pulping process chosen. Therefore, it is extremely important to re-examine the correlations before applying them for analysis of design and simulation of multiple effect black liquor evaporation system.

In addition to the above findings the present investigation intends to establish interaction with BSW system where the main variables apart from the quality of pulp are DF and number of stages, N. The BSW and MEE systems, both being discrete in nature demands a statistical correlation. As a matter of fact, no such correlations are reported till today in any literature. Therefore it is evident that establishing the parametric relationship among input and output variables of MEE systems and inter-linking relationship between MEE and BSW will enormously help to the designer and practicing engineer in a paper industry. However to proceed for the above goal to achieve one must know the MEE configuration along with the optimum number of effects.

In the present investigation, therefore, the first attempt, will be made to find out the optimum number of effects before proceeding to other areas of importance.

The present investigation deals with modeling, and simulation of multiple effect evaporator (LTV) used for the concentration of weak black liquor. Equations based on mass and energy balances and heat transfer rate have to be developed for this purpose. As the number of evaporator bodies in set increases, the solutions of the equations become increasingly difficult. For example for design of MEE of n body in a greenfield mill needs $2n+1$ equations without any equation for extra heat conservation measures like flashing of condensate and product. If one adds thermodynamic equilibrium relationship the number of equations will be still higher. For sextuple effect evaporator the total number of equations will be twelve excluding the overall mass balance. Further, the

equations are nonlinear type and even the physical properties are concentration and temperature dependent. This calls for developing a calculation procedure for design and simulation of MEE system which is to be meticulously planned before optimization. Many numerical methods are available in literature to solve such system of linear and non-linear equations. The methods for solving a set of linear algebraic equations are: Cramer's Rule, Gauss Elimination, Square Root method, Scheme of Cholesky, and iterative methods, like Gauss-Seidel method and Gauss-Jordan method etc. Many investigators(29,58,98) developed an algorithm which reduces the systems of non-linear algebraic equations that govern the evaporator system to a linear form by any means and solve them iteratively by a linear technique, e.g. Gaussian Elimination etc. These methods might have limitations as indicated by many investigators (5,17,71,72,89,126). Therefore suitable numerical method for solving such systems of nonlinear equations are essentially needed. The Newton's method and method of iteration are widely used for the above purpose. However to establish the rapidity of convergence of the Newton's process and the uniqueness of the root of the system and the stability of the process with respect to the choice of the initial approximation certain modification are made; these are: Newton-Raphson, Kantorovich, Jacobi method, Broyden method, Secant method, steepest Descent (Gradient methods) and Quasi-Newton method. Holland (42) has reported that among the above methods, the Newton-Raphson – Jacobian matrix method is the best method to solve the system of non-linear equations. Mathur (66) and Goel (29) and Singh(98) have also reported a solution procedure using Newton-Raphson method.

3.1. CORRELATIONS OF PHYSICO-CHEMICAL/ THERMAL PROPERTIES OF BLACK LIQUOR AND THEIR SELECTIONS

The modeling of Multiple effect evaporator requires mass and energy balance of the different bodies in a MEE system. These in turn depend upon characteristics of liquor, composition and physico-thermal/physico-chemical properties of liquor. The main physico-chemical / physico

thermal properties of black liquor which are pertinent to the design of evaporator system are: density (ρ), viscosity (μ), surface tension(σ) and physico- thermal properties are: specific heat(C_p), thermal conductivity(k),boiling point rise(BPR), and latent heat of vaporization(λ). These properties are, in fact, a strong function of temperature and concentration of the solids in black liquor.

The details of various properties ,their correlations and suitability are reported by Ray et al.(87). Many other information regarding other properties including viscosity are also available(33,38,50,53).

For the purpose of design calculations for multiple effect evaporator, the following correlations for physico-thermal and physico-chemical properties are chosen on the basis of their suitability. For calculation properties of steam and saturated vapor are required. All these are given in Table-3.1. These values are checked and found quite reliable even for bamboo /hardwood black liquor evaporation. It is important to mention that present investigation deals with both hardwood and bamboo black liquors.

3.2 HEAT TRANSFER COEFFICIENT

Heat transfer coefficient is also an important parameter for designing of evaporator system which in turn, is strongly influenced by physico-chemical / physico -thermal properties of black liquor.

In fact, for the accurate design of evaporator system, accurate predictions of physico-chemical/thermal properties, single and two phase pressure drop, single and two phase heat transfer coefficients, and heat flux values are essential. The system may become complicated due to the interaction of heat transfer and hydrodynamics. All the above steps are highly interactive in nature and demands iterative solutions. It is clearly mentioned that for all these interactions, the physico-chemical properties of black liquor and heat transfer parameters are required to be estimated before proceeding for **“mathematical modeling”** and

“**optimization**”. It has also been mentioned that liquor characteristics i.e. its thermodynamic, physico-chemical and rheological behavior are highly influenced by evaporator liquor flow sequences as well as the selection of evaporator types. Further, some physico-thermodynamic properties of black liquor are also required for formulation of material and energy balance and for the determination of the heat transfer coefficients from available empirical correlations.

3.2.1 Modeling Of Overall Heat Transfer Coefficient, U

It is extremely difficult to model this parameter as this is influenced by numerous process parameters including the geometrical design parameters of the equipment. In the present investigation LTV is used. A set of design data is given in Table-3.14 for LTV. The best model for estimating U for LTV till today is due to Gudmundson(33). He has developed an empirical model for estimating U based on measured data from a full scale pilot climbing film evaporator for both foaming liquid flow as well as non-foaming flow. Heat flux, liquid feed rate, subcooling, superheating of the liquid feed, boiling point of liquid and its total solid content etc. were used in the model development which were modified to suit industrial black liquor evaporator plant with standard size 8.5 m long tubes taking in to account the tube material, its thickness and possible scale on the walls of the evaporator. Coefficients of the modified equations were finally adjusted to fit 450 sets of measurement from the black liquor evaporator plants using the method of least squares with the aid of a computer. The model developed by Gudmundson (33) is reproduced below:

The parameter heat flux has been found to have the greatest effect on the value of heat transfer coefficient (HTC), U. A function is therefore defined as

$$U=f(q) = P^1 \cdot C^{P2} \cdot [P^3 \cdot q + P^4 \cdot q^2 + P^5 \cdot q^3] \quad (3.1)$$

where C is a correction factor, a product of as several terms as under:

$$C = C_{\mu} \cdot C_T \cdot C_F \quad (3.2)$$

Table- 3.1 Physico-thermal/chemical properties of black liquor, saturated steam and condensate

S.No.	Parameters	Correlations	Function Of	Ref
1.	Latent heat of vaporization, λ , J/kg	$\lambda = 2519.5 - 2.653 \times T$	Temperature	(79)
2.	Boiling point rise, BPR, K	$BPR = 41.4 \times (TS + 1)^2$ $BPR(P) = BPR \times 0.00387 (T_p^2 / \lambda_p)$	Concentration and Pressure	(87)
3.	Specific heat, C_p , J/kg K	$C_p = \{1.0 - 3.234 \times (TS / T1)\} \times 4190$, Where $T1 = (T \times 1.8 + 32)$	Temperature and concentration	(91)
4.	Thermal conductivity, k , W/Mk	$k = (0.504 - 0.282 \times TS + 1.35 \times 10^{-03}) \times 1.163$	Temperature and concentration	(38)
5.	Pressure, P , kN/m ²	$P = 3.73812 - 0.108896 \times T1 + 0.0012806 \times T1^2 - 6.69111 \times 10^{-06} \times T1^3 + 1.99203 \times 10^{-08} \times T1^4$ where $T1 = (T \times 1.8 + 32)$	Temperature	
6.	Density, ρ , kg/m ²	$\rho = 1007 - 0.495 \times T + 6.0 \times TS$	Temperature and concentration	(91)
7.	Viscosity, μ , mPas	$\mu = \exp [a + b. (TS) + c. (TS)^2 + d. (TS)^3]$ Where, $a = 0.4717 - 0.02472 \times T + 0.7059 \times 10^{-05} \times T^2$ $b = 0.06973 - 0.5452 \times 10^{-03} + 0.1656 \times 10^{-05} \times T^2$ $c = 0.002046 + 0.3183 \times 10^{-04} \times T + 0.9761 \times 10^{-07} \times T^2$ $d = 0.5793 \times 10^{-04} - 0.1629 \times 10^{-08} \times T^2$	Temperature and concentration	(50, 33)
	Enthalpy of Saturated water	$h_s = AT + B$, where $A = 4.1832$, $B = 0.127011$	Temperature	(79)
	Enthalpy of Saturated steam/vapor	$H_s = CT + D$, where $C = 1.75228$, $D = 2503.35$	Temperature	(79)

C_{μ} , C_T and C_F being the correction factors for liquor viscosity, boiling point and liquor feed respectively as given below:

$$C_{\mu}=P^6+P^7.\mu_m+P^8.\mu_m^2+P^9.\mu_m^3 \quad (1)$$

$$C_T=P^{10}+P^{11}.T_{boil}+P^{12}.T_{boil}^2+P^{13}.T_{boil}^3 \quad (2)$$

$$C_F=Z+[P^{14}+P^{15}XZ].F \quad (3)$$

Z can be calculated from the following equation.

$$Z=1.0+P^{16}.\text{Tanh}[(q-\text{Bound1})/P^{17}]xT_{sub}^{P^{18}} \quad (4)$$

Bound 1 is the limiting value in the function q, can be calculated from the following equation:

$$\text{Bound1}=P^{19}+P^{20}.\text{Log}\mu_m+P^{21}.T_{boil} \quad (5)$$

If the liquor feed temperature is superheated ,then extra vapor is flashed off in the tube which equivalent to a certain increase in the heat flux value q, which in turn can be estimated from a balance equation as given under:

$$\Delta q=T_{sup}.\text{Cp}.FD.(\pi D^2/4).c_{eff}/A \quad (6)$$

c_{eff} is an efficiency factor ,the value of this coefficient lies between 0 and 1.This value shows efficiency of the flashed vapor in comparison with corresponding increase of heat flux q.

T_{sup} is the superheating of liquor feed and is defined as:

$$T_{sup}=T_{in}-T_{max} \quad (7)$$

T_{max} is the maximum temperature of bulk liquor temperature profile along the tube and calculated as follows:

$$T_{max} = P^{22} + [P^{23} + P^{24} . T_{boil}] . F + [P^{25} + P^{26} . T_{boil}] . \text{Log}\mu_m + P^{27} . T_{boil} \quad (8)$$

At extremely low heat flux, $q < \text{Bound 2}$, where

$$\text{Bound2}=P^{28}+P^{29}.\text{Log}\mu_m+P^{30}T_{boil} \quad (9)$$

In the case when $q = 0$,the heat transfer coefficient of the liquid side, h, is calculated from the known Dittus Boelter Correlation :

- $C_{sub} = 1.0 + 0.04 \times T_{sub} \cdot [Bound\ 2 - q] / Bound\ 2]^2$

If $T_{sub} < 0$, put $T_{sub} = 0$ in the later equation.

- Calculate the overall heat transfer coefficient as under

$$U = [h + (U_{bound} - h) \times q / Bound\ 2] \times C_{sub}; \text{ when } q < Bound\ 2,$$

$$h = 0.023 \cdot Re^{0.8} \cdot Pr^{0.4} \cdot k / D$$

Computer Program

Computer programs based on Fortran-77 are now developed separately for the models for physico-thermal/ physico-chemical properties of black liquor as a function of temperature and concentration. Algorithms and computer program are also developed for overall heat transfer coefficient. These programs are used as sub-routines/sub-programs and are linked up with main program given in APPENDIX-X so that at any local value of temperature / pressure, and concentration indicated by each evaporator body of MEE system, the design properties can immediately be estimated. If the value for these design properties does not match, the steps are again repeated till a constant value is obtained.

3.3 DEVELOPMENT OF STEADY STATE MATHEMATICAL MODELS AND ITS SOLUTION

The modeling of multiple effect evaporator needs two aspects- The modeling of optimum number of effects and flow sequence. These are developed as under.

3.3.1 Development of a Total Annual Cost Equation to Find Out the Optimum Number of Effects

To initiate the modeling and simulation for Indian industry multiple effect evaporator comprising of a fixed number of bodies is to be ascertained. This needs optimization with minimum total annual cost as a decision variable. Approximate market costs of the basic items like steam, water, material of construction, labor etc will be enough for the preliminary selection of optimum number

of effects. It is however, a usual practice to determine the optimum number of effects in a system to enhance steam economy without affecting the capacity if area of the individual bodies are known. Practicing engineers in industry normally follow classical method of minimizing total annual cost comprising of fixed charges based on total capital cost Vs steam and fuel cost. It has been shown that there are many other cost components in addition to the above that can not be neglected in today's context, especially for Indian Industry(88)

It is well known to the process engineer that the larger the number of effects in a MEE, the less is the intake of steam by evaporators for the same quantum of evaporation (capacity). It appears, therefore, that for the large number of evaporator bodies the steam economy will be maximum. Economic consideration however sets a limit to the use of unlimited number of bodies.

The total annual cost of evaporation can be modeled to comprise of the following:

$$\begin{aligned}
 \text{Total cost (C}_T\text{)} = & \text{Labor (C}_L\text{), Supervision charges (C}_{SL}\text{) and Overall, laboratory and} \\
 & \text{administrative expenses (C}_{OLA}\text{) + Periodic cleaning cost (C}_C\text{)} \\
 & + \text{Fixed charges based on first cost (C}_{FC}\text{)} \\
 & + \text{Repair and maintenance charges (C}_{M-R}\text{)} \\
 & + \text{Fuel and steam charges (C}_S\text{) + Condensing and} \\
 & \text{Cooling water cost (C}_{Cw}\text{) and Charges on electrical} \\
 & \text{power (C}_P\text{).+Loss of capacity due to BPR (C}_{BPR}\text{)} \qquad \qquad \qquad (3.
 \end{aligned}$$

In the above total cost statement except the third term, i.e. C_{FC} , are normally grouped under operating charges although many investigators considered C_{M-R} and C_P as a part of fixed charges.

Each and individual cost equations are shown as under:

Labor, Supervision, Overall, laboratory and administrative charges, C_L, C_{SL}, C_{OLA}

has been taken from Aries and Newton(4), Ulrich(118) and Ray(28)

labor cost, C_L .

$$C_L = O * S * D * f_0 * P_L * n \quad (3.18)$$

supervision charges, C_{SL} .

$$C_{SL} = 0.15 * C_L \quad (3.19)$$

The overall laboratory and administrative charges can be obtained by the following equation

$$C_{LA} = (1 + 0.15) * n * S * O * D * f_0 * P_L \quad (3.20)$$

periodic cleaning cost, C_C

$$C_C = \{(n-2) + 2/K_1\} K_1 C_c (E_T/e_1) (D/R) \quad (3.21)$$

fixed charges based on first cost, C_{FC} consist of interest on investment, amortization, depreciation depending on the useful life of evaporator, taxes, insurance and other overhead charges. In actual practice, the fixed charges now thus can be modeled as

$$C_{FC} = A * (n)^b * F_1 * P_{FC} \quad (3.22)$$

repair and maintenance charges, C_{M-R} includes the cost of labor, material, and supervision, the cost of power or energy involved. In process industries this is normally expressed as a rounded off fractions of the first cost. Tube replacement and other related cost items constitute the greatest source of expense. Magnitude of these items varies greatly according to the liquor evaporated and is difficult to generalize with any degree of accuracy. An appropriate equation as developed by Ghosh and Ray (28) is as follows:

$$C_{M-R} = (M/100) * (E_T/e_1)^{0.5} * n \quad (3.23)$$

fuel and steam charges, C_S

The steam consumption is a complex function of many input parameters.

Rich(118) however suggested the following equation

$$n_s = \sum m_v / (n^y)^{2/y}$$

$$n_{v,n} = m_s y^n = \sum m_v / (n^y)^{2/y} * (y)^n$$

where m_s is steam flow rate and $m_{v,n}$ is the quantity of vapor removed from the effect. y indicates economy, equal to m_v/m_s , the value of which can be assumed to be 0.85 for black liquor evaporation without much error. The mass flow rate of vapor from the last body can be estimated from the following equation.

$$m_{v,n} = m_s y^n = \sum m_{vi} / (n^y)^{2/y} * (y)^n = \sum m_{vi} / n^{0.682} (0.85)^n \quad (3)$$

Now the C_S can be modeled as follows:

$$C_S = m_s * f_0 * P_s \quad (3)$$

In this present investigation the later equation, is used.

Models for Condensing -Cooling water cost, C_{CW} , condensing equipment, C_{CE} , air handling equipment, C_{AE} , and power cost, C_p (25,27):

The cost due to condensing, water cooling and power required consists of three types of cost viz. the equipment (condensing as well as cooling) costs, the power cost and the replacement make up water cost. It needs to calculate the cooling water requirement, equipment size of condenser as well as vacuum pump. These are estimated step by step as follows:

(a) Estimation of cooling water requirement and corresponding cost, C_{CW}

$$m_{c,w} = m_{v,n} (H_{v,n} C_{pw} t_2) / C_{pw} (t_2 - t_1) \quad (3)$$

where $m_{v,n}$ is amount of vapor, kg/h; $H_{v,n}$ is total enthalpy of vapor from last body, t_1 and t_2 are temperature of inlet and outlet water,

Putting the values of $m_{v,n}$ as $\sum m_{vi} (0.85)^n / n^{0.682}$, and other variables, one can get the following equation

$$C_{CW} = m_{c,w} * P_{Cw} * f_0 \quad (3)$$

(b) Estimation of equipment cost for condensing and injection, C_{CE}

The power cost is related directly to the water quantity involved in the condensing and cooling process. The equipment cost ($P_i + P_c$) is generally taken as proportional to the square root or

power(William's Sixth Tenth Factor) of water injection and cooling capacity required. If, for some standard equipment having vapor load capacity, $V_{std.}$, the price is kept at $(P_i+P_c)_{standard}$ one can write

$$C_{CE} = (P_i + P_c)_{Std} (F+f) [\sum m_{vi}(y)^n W/ n^{(y)2/y} V_{Std}]^{0.6} \quad (3.28)$$

(c) Equipment cost for Air handling equipment(C_{AE})

Total cost for condensing, cooling and the air injection system can be written in terms of cost per unit water load in injection and condensing system as:

$$C_{AE} = P_{a std.}(F+f) \{ (1.43 \sum m_{vi} a_l/24) + (\sum m_{vi} y^n Jw a_5/24 n^{(y)2/y})^{0.6} (1/V_{a std.})^{1/2} \} \quad (3.29)$$

Cost due to BPR

Cost due to BPR is given as:

$$C_{BPR} = 1/n \sum X_{av} P(n)^b (F+f) \quad (3.30)$$

3.3.2 Total Annual Cost Model, C_T

Putting all the model equations for various cost terms , one can obtain

the total annual cost of evaporation C_T as:

$$C_T = C_{OLA} + \{ (n-2) + 2/K_1 \} K_1 C_c (E_T/e_1) (D/R) + A * (n)^b * F_1 * P_{FC} + (M/100) * (E_T/e_1)^{0.5} * n + m_s * f_0 * P_s + m_{clw} * P_{Cw} * f_0 + (P_i + P_c)_{Std} (F+f) [\sum m_{vi}(y)^n W/ n^{(y)2/y} V_{Std}]^{0.6} + P_{a std.}(F+f) \{ (1.43 \sum m_{vi} a_l/24) + (\sum m_{vi} y^n Jw a_5/24 n^{(y)2/y})^{0.6} (1/V_{a std.})^{1/2} \} + 1/n \sum X_{av} P(n)^b (F+f) \quad (3.31)$$

To get optimum number of effects, the values of various cost factors and other parameters are needed. These are summarized in Table-3.2. It is important to indicate that these data are very conservative, approximate and gives order of magnitude values only to determine the optimum number of effects so that the modeling of the system can be initiated.

Table -3.2 Approximate values of cost terms

S.No.	Cost Term/Constants	Values	S.No.	Cost Term/Constants	Values
1	B	0.75	11	A, m ²	400.0
2	C _C , Rs./m ²	14	12	F	0.25
3	P _{FC} , Rs/m ²	40000.0	13	F	0.35
4	C _L , Rs/8h	250	14	E ₁ , kg/m ² h	130
5	C _{pa} , Rs./kg of water	1.63E-05	15	K ₁	0.15
6	C _{pc} , Rs./kg of water	3.42E-05	16	R	0.10
7	C _{pi} , Rs./kg of water	3.55E-05	17	R	15
8	C _s , Rs./Tonne	400	18	W, kg/kg	60
9	C _w , Rs./m ³	0.0005	19	Y	0.85
10	D, Days/year	300	20		

Knowing the values of parameters and constants as given in Table-3.2, each and every contributing term given in Eqs. 3.17-3.31 can be evaluated provided the process and design parameters of evaporator system concentrating black liquor of paper Industry are assumed. They are needed to find out not only the performance of evaporator in terms of capacity and economy but also the estimation of many cost contributing terms and their influence in total annual cost. The pertinent parameters required to do the above calculation are depicted in Table-3.2.

3.3.3 Development of Computer Programs for Optimum Number of Effects

A computer program based on also FORTRAN 77 has been developed to estimate the individual costs as well as the total annual cost (APPENDIX-X). These are shown in Table-3.3.

Table -3.3 Annual total cost, C_T

S.NO.	No. of Effects, N	Total Annual Cost, $C_T \times 10^7$ (Rs./Year)
1.	1	45.00
2.	2	30.00
3.	3	24.80
4.	4	22.50
5.	5	21.50
6.	6	21.20
7.	7	21.30
8.	8	21.50
9.	9	22.10

The relative contribution of various terms to the total annual cost can be found by closer scrutiny of the results. This is shown in Table-3.4.

Table-3.4 Percent contribution of different cost factors towards total annual costs for a sextuple effect evaporator for paper industry.

C_L	C_{SL}	C_{OLA}	C_{FC}	C_{CW}	C_s	C_C	C_{R-M}	C_{CE}	C_{AE}	C_{BPR}	C_T
0.279	0.0418	0.279	27.20	.123	60.57	0.49	9.5	0.355	.029	1.216	100

From the Table-3.4, it is interesting to note that the major item is the steam charges followed by the fixed cost. Other costs together will contribute to a maximum extent of approximately 12%

only. Cost of air handling equipment and that due to cooling water are insignificant and hence be ignored. However cost connected with the loss of heating surface area due to BPR, condenser equipment cost, cleaning cost and the total labor-supervision-overall administrative charges combined gives on an average 2.5%. Hence they should not be neglected in actual calculation at least in today's environment as approximately 1.9 million rupees are contributed by these items annually.

A graph has been plotted to show the variation of total annual cost as a function of number of effects (Fig.1). The profile displays a unimodal function and exhibits one sharp inflexing point at a minimum. Beyond this the annual cost becomes again higher. This minimum annual cost corresponds to six number of bodies, thus indicating sextuple effect evaporator is the most feasible MEE set for this present investigation for paper industry.

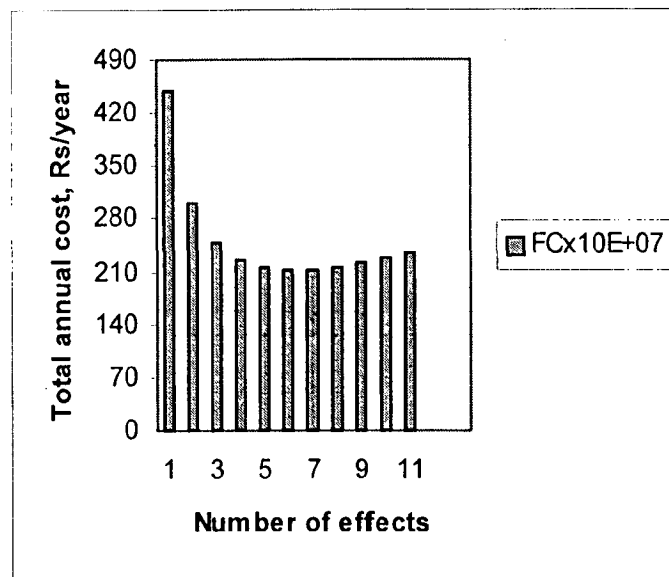
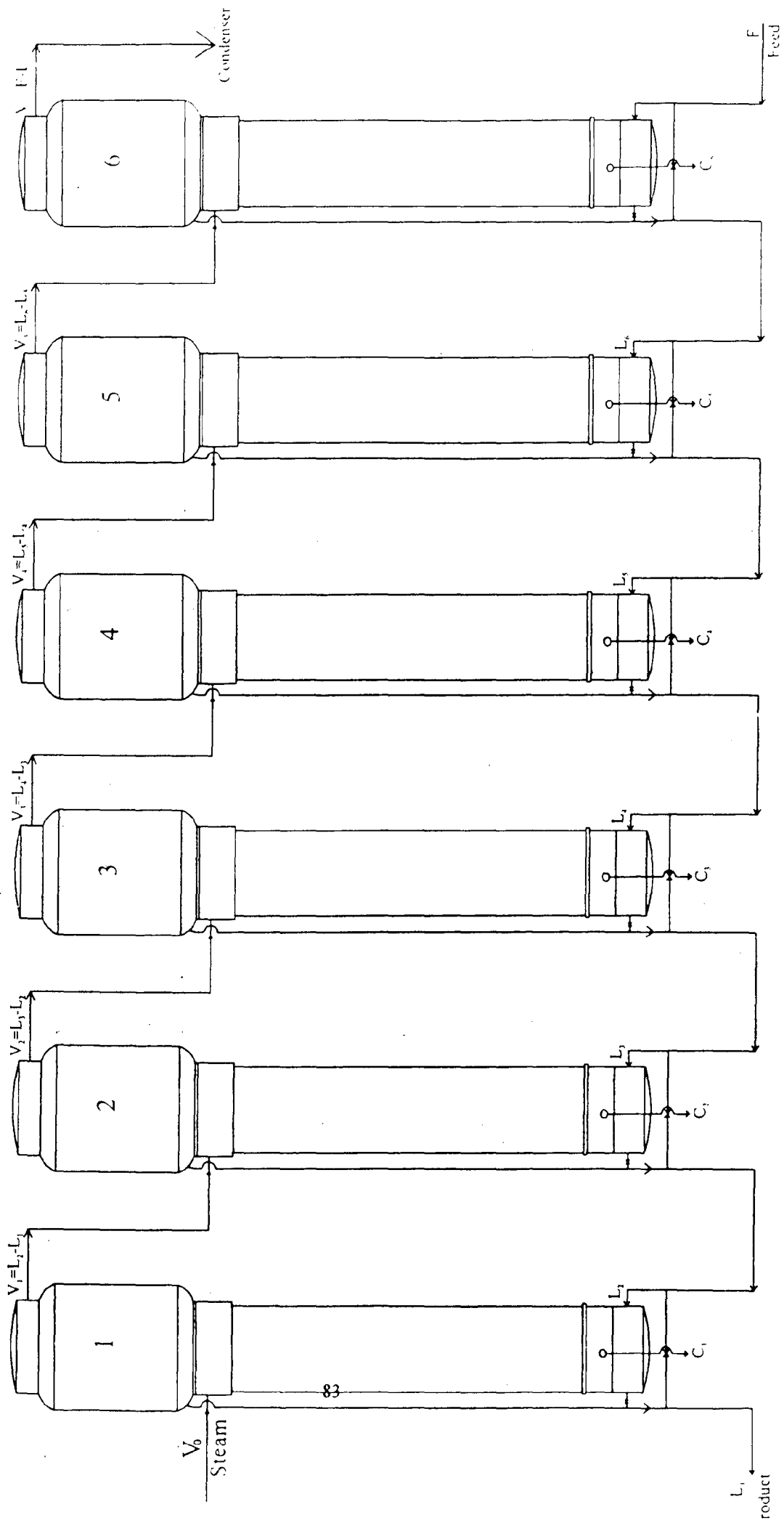


Fig.1 Total annual cost as a function of number of effects

Hence we need to develop models for six effect multiple effect evaporator for Indian industry. A diagrammatic sketch for this system is shown in Fig.3.0.



Therefore, in the present chapter, steady state model have been developed for sextuple evaporator system for paper industry in the following sections:

3.3.4 Mathematical Model for a Sextuple Effect Evaporator System With Backward I (6→5→4→3→2→1)

The steady state model of a multiple effect evaporator system include overall as well as component mass balance equations, energy balance equations, heat transfer rate equations for area calculation for all the bodies in the set-up.

These are shown in detail below for the first body and a general equation for any number of bodies in the set-up:

(a) Mass and Energy Balance Equations Around First Effect of Evaporator

A. Total mass balance equation:

$$L_2 = V_1 + L_1 \quad (3.32)$$

B. Component mass balance:

$$L_2 X_2 = L_1 X_1 \quad (3.34)$$

C. An enthalpy balance:

$$\begin{aligned} Q_1 &= V_0 H_0 - C_1 h c_1 \\ &= V_0 (h c_1 - \lambda_0 + C P v B P R_0) - C h c_1 \\ &= V_0 \lambda_0 + V_0 C P v B P R_0 \end{aligned} \quad (3.35)$$

D. Heat transfer rate:

$$Q_1 = U_1 A_1 (\Delta T_1)_{\text{eff}}$$

$$\text{Where, } (\Delta T_1)_{\text{eff}} = \Delta T_1 - B P R_1$$

$$= T_s - T_1 - B P R_1$$

Hence

$$Q_1 = U_1 A_1 (T_s - T_1 - B P R_1) \quad (3.36)$$

E. Total mass balance on the steam chest:

$$C_1 = V_0 \quad (3.37)$$

F. An enthalpy balance on the process:

$$L_2 h_2 + Q_1 = V_1 H_1 + L_1 h_1 \quad (3.38)$$

Substituting the value of V_1 from Eq.(3.32) and Q_1 from Eq.(3.35) into Eq.(3.38) gives

$$L_2 h_2 + V_0 H_0 - C_1 h_{c1} - (L_2 - L_1) H_1 - L_1 h_1 = 0$$

Adding and subtracting $L_2 h_1$ in above Eq., one can get

$$L_2 h_2 - L_2 h_1 + V_0 H_0 - C_1 h_{c1} + L_2 h_1 - (L_2 - L_1) H_1 - L_1 h_1 = 0$$

$$L_2(h_2 - h_1) + V_0 H_0 - C_1 h_{c1} - (L_2 - L_1)(H_1 - h_1) = 0 \quad (3.39)$$

Putting $h_j = CP_j (T_j + BPR_j)$,

$$H_j = h_{c_{j+1}} + \lambda_j + CP_v BPR_j \text{ and } h_{c_{j+1}} = AT_j + B,$$

Putting the values of h_j , H_j and h_{c_j} in Eq.(3.39) the following equations are developed which on simplification gives Eq.(3.40).

$$L_2 \{ CP_2 (T_2 + BPR_2) - CP_1 (T_1 + BPR_1) \} + V_0 (h_{c1} + \lambda_0 + CP_v BPR_0) - C_1 h_{c1} - (L_2 - L_1) \{ (h_{c2} + \lambda_1 + CP_v BPR_1) - CP_1 (T_1 + BPR_1) \} = 0$$

$$L_2 \{ CP_2 (T_2 + BPR_2) - CP_1 (T_1 + BPR_1) \} + (V_0 - C_1) h_{c1} + V_0 (\lambda_0 + CP_v BPR_0) - (L_2 - L_1) \{ (h_{c2} + \lambda_1 + CP_v BPR_1) - CP_1 (T_1 + BPR_1) \} = 0$$

$$L_2 \{ CP_2 (T_2 + BPR_2) - CP_1 (T_1 + BPR_1) \} + V_0 (\lambda_0 + CP_v BPR_0) - (L_2 - L_1) \{ (\lambda_1 + CP_v BPR_1) - CP_1 (T_1 + BPR_1) \} - (L_2 - L_1)(AT_1 + B) = 0 \quad (3.40)$$

f_1 is now defined as:

$$f_1 = L_2 \{ CP_2 (T_2 + BPR_2) - CP_1 (T_1 + BPR_1) \} + V_0 (\lambda_0 + CP_v BPR_0) - (L_2 - L_1) \{ (\lambda_1 + CP_v BPR_1) - CP_1 (T_1 + BPR_1) \} - (L_2 - L_1)(AT_1 + B) \quad (3.41)$$

Now from Eq.(3.35) and Eq.(3.36)

$$U_1 A_1 (T_s - T_1 - BPR_1) - V_0 (\lambda_0 + CP_v BPR_0) = 0 \quad (3.42)$$

Effect No.6

$$g_{11} = \frac{T_s}{\lambda_0} \left\{ CP_f \left(u_f + \frac{BPR_f}{T_s} \right) - CP_6 \left(u_6 + \frac{BPR_6}{T_s} \right) \right\} + \frac{(I_6 - I_5)}{\lambda_0} (\lambda_5 + CP_v BPR_5) - \frac{(1.0 - I_6)}{\lambda_0} \left\{ (\lambda_6 + CP_v BPR_6) - CP_6 T_s \left(u_6 + \frac{BPR_6}{T_s} \right) \right\} - \frac{(1.0 - I_6)}{\lambda_0} (A u_6 + B/T_s) T_s \quad (3.65)$$

$$g_{12} = \frac{U_6 T_s a_6}{50 \lambda_0} \left\{ u_5 - \left(u_6 + \frac{BPR_6}{T_s} \right) \right\} - \frac{(I_6 - I_5)}{\lambda_0} (\lambda_5 + CP_v BPR_5) \quad (3.66)$$

Before proceeding for the complete selection of the variables, one should find out the degree of freedom of this system.

Degree of Freedom

The degrees of freedom of a processing system are the independent variables that must be specified in order to define the any process completely. These are crucial for the design of the evaporator system working under both dynamic and static conditions.

The total number of independent equations describing an evaporator series of N stages is 4N. The total number of variables is the sum of N+1 vapor streams, N+1 liquid streams, N+1 pressure specifications, N+1 temperatures(an equilibrium relationship is used so that $T_L = T_V$ in each stage ; BPR is not considered), N+1 composition specifications, and N area ratios(the area of each effect). N composition variables are not independent, since T and P(pressure) are fixed at the boiling point. Thus, 5N+5 variables exist with only 4N equations. The design parameters that need to be specified in order to obtain a unique solution to the problem must then be total N+5.

Since area is a design variable, the area of each stage, A_i , is itself not normally specified, but the ratios of the area of each stage to some reference area, A, can be. One of the most common way to do this is to assume the ratios all equal to 1.0(the constant- area assumption). The reference area then becomes a dependent variable to be solved for. Specifying the ratios eliminates N-1 variables

The concentration terms X in each effect of the evaporator is related to component mass balance equation for the solute which may be stated in the following form

$$FX_i = I_j X_j \quad (j=1,2,\dots,6)$$

As a result the 4N equations needed for sextuple effect evaporator have been reduced to smaller number of equations. Therefore, we have twelve non-linear equations and twelve unknown variables. In the set of twelve non-linear equations the specified variables are latent heat of vaporization(λ), boiling point rise(BPR) and specific heat(C_p) etc. These variables can be calculated from different relations and correlations given in Table-3.2

3.4 SOLUTION PROCEDURE

It has been found in Section.3.3.3 that the optimum number of effects for concentrating black liquor are found to be six(Fig.1). Therefore, sextuple effect is to be employed for black liquor evaporation in this present investigation. For this the mathematical models have been developed in Section 3.3.4. For demonstration purposes, the solution of the set of twelve non-linear equations is developed for the design of Sextuple Effect Evaporator system . In the present investigation , we developed the mathematical models for the system using backward feed . Assuming at the initial iteration the evaporation rates and area are equal .

$$v_j = v \quad (1 \leq j \leq 6) \quad (3.67)$$

$$a_j = a \quad (1 \leq j \leq 6) \quad (3.68)$$

The various known, unknown and specified variables involved in the considered mathematical model equations are treated. These variables are classified as given below:

Known Variables:

1. Liquor feed rate = F
2. Liquor feed temperature = T_f
3. Liquor feed concentration = X_f

- 4. Steam temperature = T_s
- 5. Last effect saturated temperature = T_1
- 6. Product concentration = $X_p(X_1)$

Specified Variables:

- 1. Overall heat transfer coefficients- U_1, U_2, U_3, U_4, U_5 and U_6
- 2. Boiling point rise (BPR) - $BPR_1, BPR_2, BPR_3, BPR_4, BPR_5$ and BPR_6

Unknown Variables:

- 1. Scaled vapor flow rate - v_0
- 2. Scaled liquor flow rate - l_2, l_3, l_4, l_5 and l_6
- 3. Scaled temperature - u_1, u_2, u_3, u_4 and u_5
- 4. Fractional heating area- a and
- 5. Concentration - X_2, X_3, X_4, X_5 and X_6

The concentration terms X in each effect of the evaporator is related to component mass balance equation for the solute which may be stated in the following form

$$FX_f = l_j X_j \quad (j = 1, 2 \dots 6) \quad (3)$$

Therefore, we have twelve non-linear equations (from Eqs. 3.55 to 3.66) and twelve unknown variables. These equations can be solved simultaneously by numerical method for the two unknowns.

In this present case numerical techniques using the globally convergence characteristics method Newton-Raphson – Jacobian matrix to solve the system of non-linear equations developed through models of black liquor multiple effect evaporator might be more effective and reliable. This method is already tested and found to be more reliable and efficient than the well known Broy method. Newton-Raphson method converges rapidly to the desired accuracy. The algorithm

simple, easy to program, inherently stable and virtually guaranteed convergence, thereby eliminating the biggest problems with general nonlinear methods.

Before taking up the application of the model to a typical MEE system in paper industry, it is prudent to highlight some salient features of the Newton-Raphson method.

3.5 Newton-Raphson Method

The extension of the method of Newton to functions of several variables is called the Newton-Raphson method. It is developed in a manner analogous to that known for Newton's method. The Newton-Raphson method consists of the repeated use of the linear terms of the Taylor series expansions of the functions $g_1, g_2, g_3, \dots, g_{12}$ [Eqs(3.55) through (3.66)]; namely,

$$\begin{aligned}
 0 = g_j &+ \frac{\partial g_j}{\partial v_0} \Delta v_0 + \frac{\partial g_j}{\partial u_1} \Delta u_1 + \frac{\partial g_j}{\partial u_2} \Delta u_2 + \frac{\partial g_j}{\partial u_3} \Delta u_3 + \frac{\partial g_j}{\partial u_4} \Delta u_4 + \frac{\partial g_j}{\partial u_5} \Delta u_5 \\
 &+ \frac{\partial g_j}{\partial l_2} \Delta l_2 + \frac{\partial g_j}{\partial l_3} \Delta l_3 + \frac{\partial g_j}{\partial l_4} \Delta l_4 + \frac{\partial g_j}{\partial l_5} \Delta l_5 + \frac{\partial g_j}{\partial l_6} \Delta l_6 + \\
 &\frac{\partial g_j}{\partial a} \Delta a
 \end{aligned} \tag{3.70}$$

(j = 1, 2, 3, ..., 12)

where

$$\Delta v_0 = v_{0, (k+1)} - v_{0, k};$$

$$\Delta u_1 = u_{1, (k+1)} - u_{1, k};$$

$$\Delta u_2 = u_{2, (k+1)} - u_{2, k};$$

$$\Delta u_3 = u_{3, (k+1)} - u_{3, k};$$

$$\Delta u_4 = u_{4, (k+1)} - u_{4, k};$$

$$\Delta u_5 = u_{5, (k+1)} - u_{5, k};$$

$$\Delta l_2 = l_{2, (k+1)} - l_{2, k};$$

$$\Delta l_3 = l_{3, (k+1)} - l_{3, k};$$

$$\Delta l_4 = l_{4, (k+1)} - l_{4, k};$$

$$\Delta l_5 = l_{5, (k+1)} - l_{5, k};$$

$$\Delta l_6 = l_{6, (k+1)} - l_{6, k};$$

$$\Delta a = a_{, (k+1)} - a_{, k};$$

and where the subscripts are kth and k + 1st trials. The seventeen non-linear equations may be stated in compact form by means of the given matrix equation :

$$J_k \Delta X_k = - g_k \tag{3.71}$$

where J_k is called the Jacobian matrix of order 12 . ΔX_k and g_k are conformable vectors.

A display of the elements of J_k , g_k and X_k follows:

$$J_k = \begin{bmatrix} \frac{\partial g_1}{\partial v_0} & \frac{\partial g_1}{\partial u_1} & \frac{\partial g_1}{\partial u_2} & \dots & \frac{\partial g_1}{\partial m_5} & \frac{\partial g_1}{\partial a} \\ \frac{\partial g_2}{\partial v_0} & \frac{\partial g_2}{\partial u_1} & \frac{\partial g_2}{\partial u_2} & \dots & \frac{\partial g_2}{\partial m_5} & \frac{\partial g_2}{\partial a} \\ - & - & - & \dots & - & - \\ - & - & - & \dots & - & - \\ - & - & - & \dots & - & - \\ - & - & - & \dots & - & - \\ \frac{\partial g_{12}}{\partial v_0} & \frac{\partial g_{12}}{\partial u_1} & \frac{\partial g_{12}}{\partial u_2} & \dots & \frac{\partial g_{12}}{\partial m_5} & \frac{\partial g_{12}}{\partial a} \end{bmatrix} \tag{3.72}$$

$$\text{and } g_k = [g_1 \ g_2 \ g_3 \ \dots \ g_{12}]^T \tag{3.73}$$

$$\Delta X_k = X_{k+1} - X_k \tag{3.74}$$

$$X_k = [v_0 \ u_1 \ u_2 \ u_3 \ u_4 \ u_5 \ l_2 \ l_3 \ l_4 \ l_5 \ l_6 \ a]^T \tag{3.75}$$

$$X_k = [\Delta v_0 \ \Delta u_1 \ \Delta u_2 \ \Delta u_3 \ \Delta u_4 \ \Delta u_5 \ \Delta l_2 \ \Delta l_3 \ \Delta l_4 \ \Delta l_5 \ \Delta l_6 \ \Delta a]^T \tag{3.76}$$

The subscripts k and k + 1 denote that elements of the matrices carrying these subscripts are those

given by the k th and $k + 1^{\text{st}}$ trials, respectively. For simplicity, the subscript k is omitted from the elements of the X_k , J_k and g_k .

On the basis of an assumed (initial) set of values for the elements of the column matrix $X_k (= X_0)$ the corresponding values of the elements of J_k and g_k are computed.

The computed values of J_k and g_k are used to calculate the values of X_k , by solving Eq.(3.71) using Gauss elimination method with partial pivoting supplemented with LU decomposition. Subsequently, X_{k+1} is calculated from Eq.(3.74) for its use in the next trial. This procedure is repeated until the desired accuracy of the values of unknown variables is obtained.

3.5.1 Sufficient Conditions for the Convergence of Newton Raphson Method

Assuming that the solution set of the independent variables be represented by the column vector α

$$\alpha = [\alpha_1, \alpha_2, \alpha_3, \dots, \alpha_{11}, \alpha_{12}]^T \quad (3.77)$$

it implies that

$$f_i(\alpha) = 0 \quad (i=1,2, 3, \dots, 11,12) \quad (3.78)$$

Or
$$g(\alpha) = 0$$

The elements of g_k and J_k are considered to be continuous over all starting vectors X_0 and all vectors X_k generated thereafter by the use of the **Newton-Raphson** method. Further, if the determinant of J_k is non zero ($|J_k| \neq 0$) for all values of X_k , including X_0 , it can be demonstrated that when the starting vector X_0 is “close” to the solution vector α , the Newton Raphson converges to the solution vector α . Here “close” means that the product of the **Hilbert norms of the matrices** required to relate the **error vectors** E_k and E_0 is less than unity, where the error vectors are given by $E_k = X_k - \alpha$ and $E_0 = X_0 - \alpha$.

In the present work, the **Jacobian matrix** is generated numerically. For this a perturbation of magnitude 0.01 in column vector X_k is applied and subsequent values of g_k are computed to

form J_k . The tolerance selected for variables $v_0, u_1, u_2, u_3, u_4, u_5, l_2, l_3, l_4, l_5,$ and a . The functions to g_{12} is taken to be 0.000001 for an acceptable solution.

3.6 DEVELOPMENT OF COMPUTER PROGRAM FOR SEXTUPLE EFFECT EVAPORATOR

The steady state models developed in Section-3.3.4 are now to be subjected to MEE system with an aim to calculate the steam flow rate, steam economy and area requirement. In other words how much economy can be at any operational condition of MEE. This procedure thus helps to conserve energy for the paper industry. It has already been mentioned that the process is very complex due to many parameter interactions and their inter-dependency. In today's context it is extremely essential to use this software for the benefit of industry, paper mill in particular. It is practically impossible to do by hand calculation using classical iterative trial technique.

In this present investigation again FORTRAN-77 Programs have been developed specially for the above purpose using HCL-HP Pentium PC. The computer program for backward feed flow sequence is given in APPENDIX-X. A typical set of results is depicted in Table-1 of APPENDIX VII.

3.7 RESULTS AND DISCUSSION

It has also been emphasized in Chap-1 that the design and operational parameters (tube dimensions, velocity of liquor, feed rate, temperature and pressure) are equally important for modeling of MEE. A set of operational data normally employed in the paper industry globally given in Table-3.5. With this data along with the equations for physico-chemical/thermal properties already depicted in Table-3.2 and the developed models for a given number of stages of MEE, the calculation procedure structured in this study computes design variables such as area (or area ratio between effects), externally supplied steam rate, stage temperature, flow rates of liquids and vapors and finally steam economy. The range of operational parameters is depicted in Table-3.6.

The logical sequence of calculation for multiple effect evaporation system for black liquor concentration is shown below in terms of flow chart:

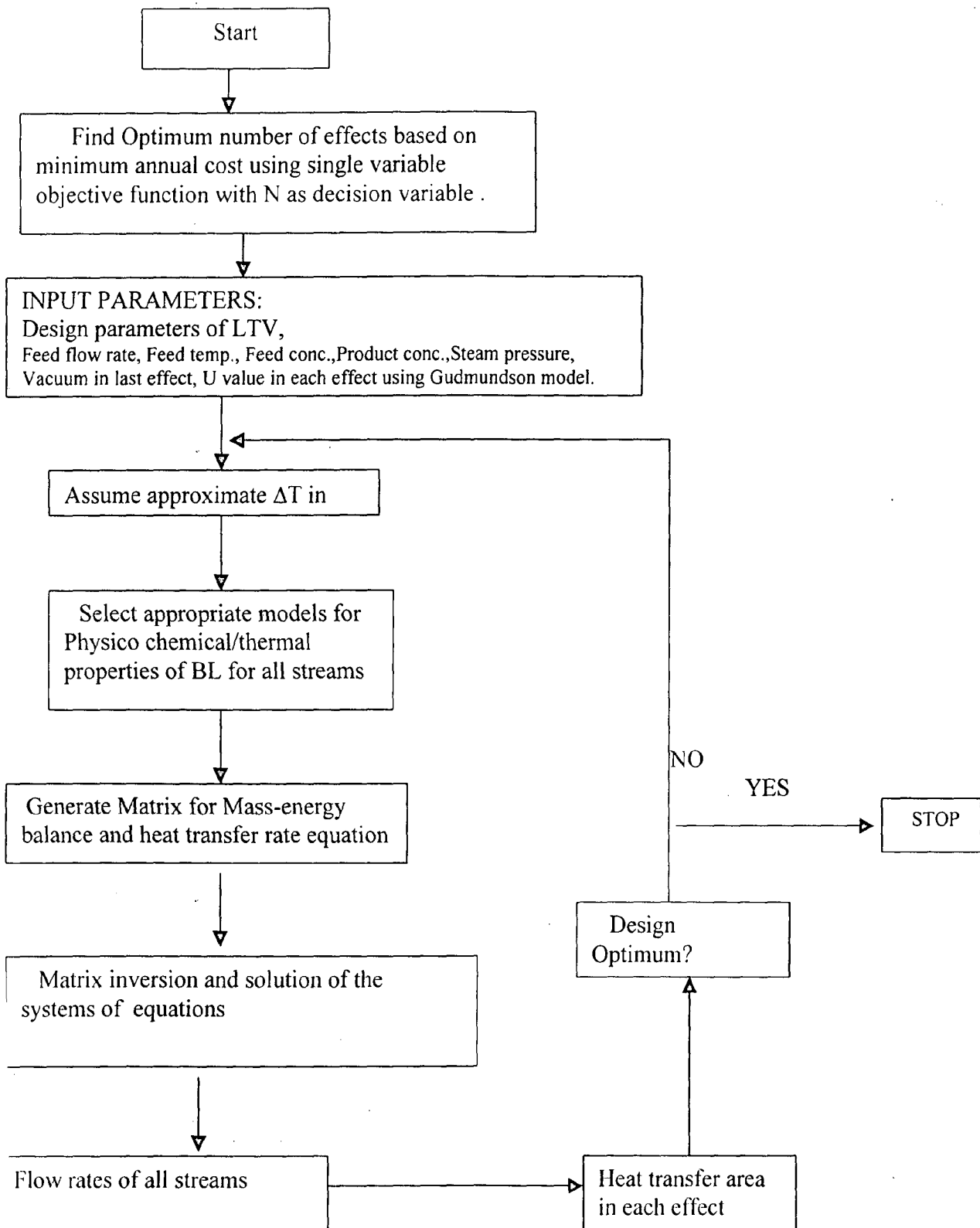


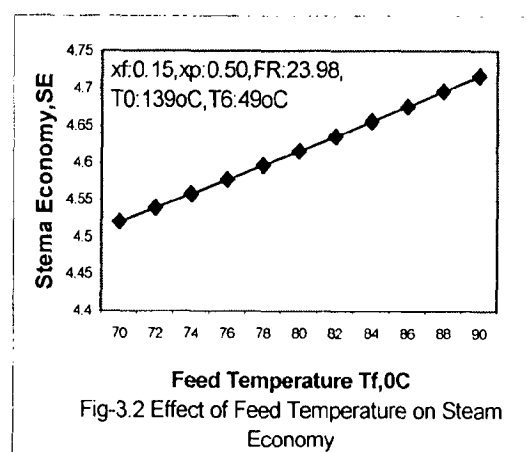
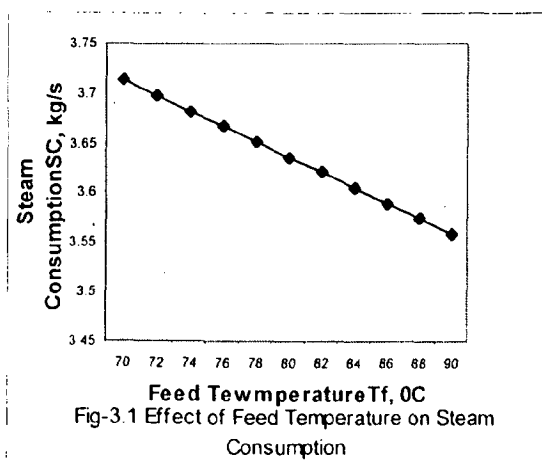
Table - 3.6 Range of operational parameters

S.No.	Operational Parameter	Parameter's Range	Interval
1.	Liquor feed flow rate, kg/s	18.00-25.00	1.00
2.	Liquor feed temperature, °C	70.00-90.00	2.0
3.	Liquor feed concentration	0.10-0.17	0.01
4.	Steam temperature, °C	135-140	1.0
5.	The last body saturation	48-52	1.0
6.	Liquor product concentration	0.48-0.52	0.01

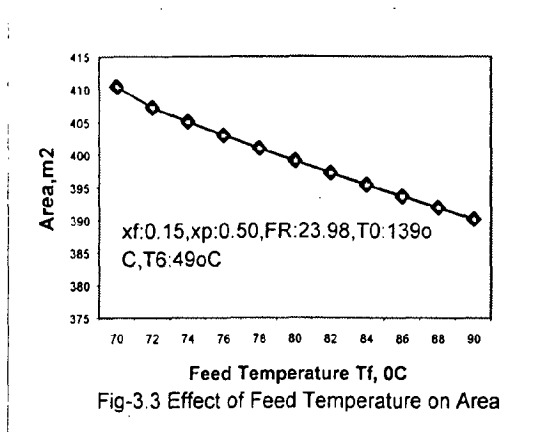
The results obtained from the model are plotted in graphs and the parametric influences interpreted. The effect of various input parameters on output parameters i.e.st consumption(SC),steam economy(SE) and area requirement(A) for backward feed sequenc described in the following paragraphs.

3.7.1. Effect of Feed Temperature on Steam Consumption(Sc), Steam Economy(Se) Area Requirement(A)

Fig. 3.1 to 3.3 have been drawn to show that the effect of feed temperature on output param



namely, steam consumption(SC), steam economy (SE), and area (A) respectively for backward feed sequence. In these plots specified variables are feed flow rate F, feed concentration X_F and final product concentration X_p , steam temperature T_O , last effect temperature T_N . With the rise of feed temperature decrease in SC, increase of SE and rapid decrease of A are noticed.



It is evident from the Figs. that SC and SE Vs T_f are strongly linear whereas area Vs T_f plot slightly non linear for the same feed and product concentration, feed flow rate, and steam and last body temperature. On closer scrutiny of the results and the curve it is clearly visible that with the $10^\circ C(70-80^\circ C)$ decrease of SC, increase of SE, decrease of area requirements are of the order of 2.07%, 2.1.1%, 2.77% respectively.

Further increase in temperature from $(80-90^\circ C)$, the same values evaluated are 2.13%, 2.19%, 2.24% respectively. The above results are summarized in the following Table.

Table-3.7 Effect of feed temperature on SC, SE and A.

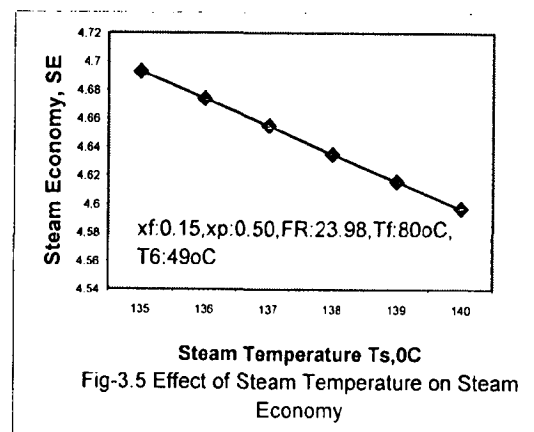
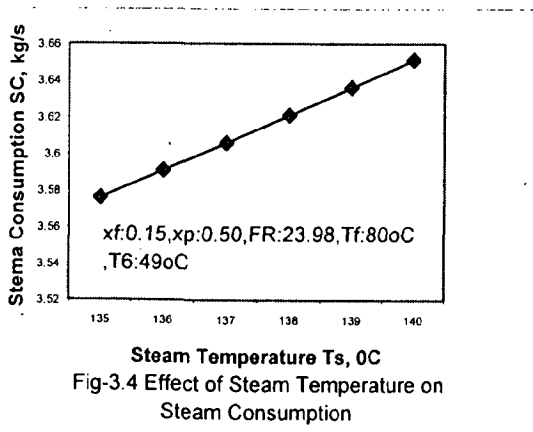
$\Delta T_f, ^\circ C$	SC, %	SE, %	A, %
70-80	2.07	2.101	2.77
80-90	2.13	2.19	2.24
Average, $10^\circ C$	2.1	2.15	2.505

Thus substantial gain have been obtained if one increases the temperature of feed above 70⁰C still more if above normal temperature of feed around 80⁰C. Therefore any temperature betw 70-90⁰C can be kept for the above benefits in terms of decrease in steam consumption(SC) reduced demand of heating area requirements.

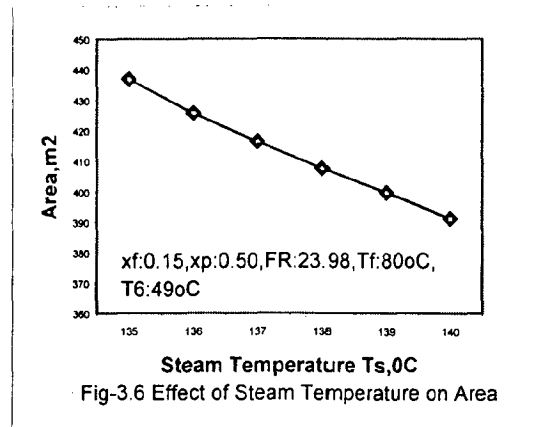
Normally in industry keeping maintaining temperature above 80⁰C becomes difficult becaus exposure of hot black liquor to atmosphere during Melone Filter operation. Generally the pulp liquors first go to a storage tank and then to fiber filter operation and successive transporta through pipelines to the weak black liquor storage tank and finally to MEE. Therefore, using 8 as feed temperature is quite justifiable. However if it is possible to maintain $T_f = 90^0C$ without of heat much more benefits can be obtained in terms of capital expenditure(area) and st consumption. Assuming some heat losses in the above black liquor handling systems. One proceed for optimization with 80⁰C of feed temperature which is considered quite reasonable f practical point of view.

3.7.2. Effect of Steam Temperature on Steam Consumption(Sc), Steam Economy(Se) Area Requirement(A)

Steam temperature T_s is another important parameter for prediction of evaporator design and performance. Fig. 3.4-3.6 have been plotted with steam consumption(SC), steam economy(



requirement(A) as a function of T_s with T_f at 80°C . Normally in industry the temperature is kept between 125°C (134.10 kN/m^2)- 150°C (378.1755 kN/m^2). However, most of the Indian Industry work between 130 - 140°C . Therefore the figures have been drawn for steam consumption(SC),



steam economy(SE) and area with temperature of steam varying between 135 - 140°C , while the other parameters are kept constant and feed temperature is assumed as 80°C as explained in the previous paragraph. Scaling becomes a more severe problem at high surface temperatures above 145°C which can be lessened by keeping the condensing steam temperature below 135 - 143°C (30).

On inspection of the curves and data is found that steam consumption increases with the increase of steam temperature(steam pressure), decrease of steam economy both exhibiting linear characteristics but decrease of area requirement with slightly concavity upwards. It is a fact that use of high steam pressure(high temperature) decreases steam economy and increases steam consumption . This is caused partly due to higher temperature level in the evaporator and partly by lower latent heat of steam at high pressures. This becomes more detrimental when evaporator becomes scaled and the steam pressure has to be increased to maintain evaporator capacity with consequent decrease in steam economy. This is further explained by the fact that calcium scaling in black liquor evaporator is extremely temperature sensitive. The Arrhenius activation energy of

60-70kCal/mole is usual which corresponds to the rate doubling for every 2.8-3.9⁰C temper. rise(30). It is known from the literature (30) that below liquor temperature of about 125⁰C or s temperature of about 138⁰C calcium carbonate scaling is not a major problem. The solubili sulphate , carbonate and burkeite(2Na₂SO₄, Na₂CO₃) is nearly independent of temperature in range 100-140⁰C and is not greatly influenced by the liquor organics.

With the rise of steam temperature of 5⁰C the steam consumption increases by nearly 2.0 decrease of steam economy of the order of 2.05% and decrease of area requiremer approximately 10.5%. Therefore increases of steam temperature is beneficial in terms of ca cost(area requirement) but steam consumption will be higher enhancing operating cost. A bal between the two i.e. decrease of area requirement Vs steam demand has to be optimized. known from literature that some of the scales particularly water insoluble calcium scale is sens to steam temperature rise compared to concentration effect. Therefore temperature around 139⁰ quite acceptable.

The results are summarized in the following Table.

Table-3.8 Effect of steam temperature on SC, SE and A.

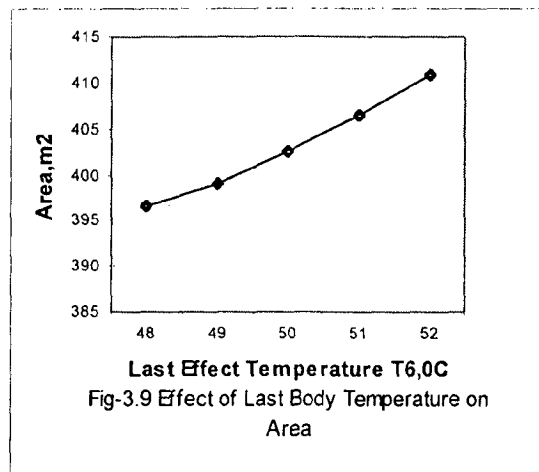
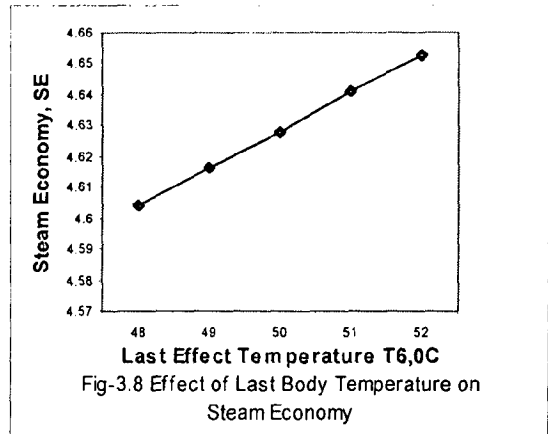
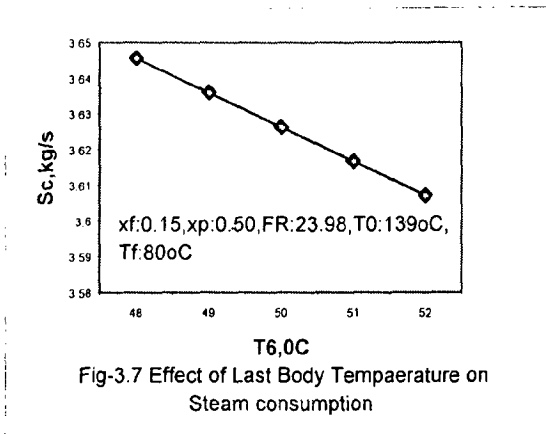
$\Delta T_s, ^\circ C$	SC,%	SE, %	A, %
135-140 ⁰ C	2.09	2.045	10.49

It is advisable that temperature should not exceed above 140⁰C.

3.7.3. Steam Consumption(Sc), Steam Economy(Se) and Area Requirement(A) as a Func of Last Body Temperature(T₆)

Last body temperature(vacuum) is equally essential parameter for evaporator operation. In present investigation the last body temperature is varied between 40⁰C – 50 ⁰C . It is well kn that most of the Indian industries are working with this temperature range.

Figs. 3.7 – 3.9 show the influence of last body temperature (and vacuum) as a parameter keeping the temperature of feed at 80°C and steam temperature at 139°C while other parameters remaining constant. On examining the plots it reveal that there is a sharp decrease of SC and SE and increase of area demand. For 4 °C rise of last body temperature(and lowering vacuum), decrease of steam consumption , increase of steam economy on the order of nearly 1 % where as area increase will



be on the order of 3.6% are observed. From investment point of view decrease of SC(operational cost) and increase of area demand(capital cost) are both detrimental. Hence at any cost decrease of vacuum , increase of temperature at the last body should not be allowed. In the present study

49°C(11.77 kN/m²) temperature of last body are considered adequate for better economy ,low steam consumption and lower area requirement.

The results are depicted in the following Table.

Table-3.9 Effect of last body temperature on SC, SE and A.

$\Delta T_6, ^\circ\text{C}$	SC, %	SE, %	A, %
48-52 ⁰ C	1.06	1.06	3.56

3.7.4. Influence of Product Concentration on Steam Consumption(Sc), Steam Economy and Area Requirement(A)

The total solids concentration of the discharged liquors from MEE influences the steam economy and steam consumption and also area demand.

Figs. 3.10- 3.12 show the influence of product concentration on SC, SE, and area demand A. product concentration is however varied between 48% -52%. This range is most accepted range practice in Indian mills. Usually industry keeps the value in a close range between 48%-52%. Above 50 % solids concentration, the transportation problem is experienced with Indian b liquors.

It is reflected from the figures that all the parameters ,namely, SC, SE and A increase very sharply with product concentration. Though SE Vs X_p plot is clearly linear the same for SC and A exhibits slightly non-linear curvature. SC increases on the order of nearly 0.6% while SE and A increases of the order of 2.88% and 7.42% respectively. These are expected behavior(30, 43). If the discharged liquor concentration is lowered, the steam economy decreased. This is caused by the fact that more liquor is pumped through the evaporator in relation to the evaporation rate. The additional liquor must be heated to the boiling point in the evaporator effects and less heat is available to cause evaporation.

(43)

Hence in this present investigation standard product concentration 50% is considered appropriate for analysis and design of black liquor MEE.

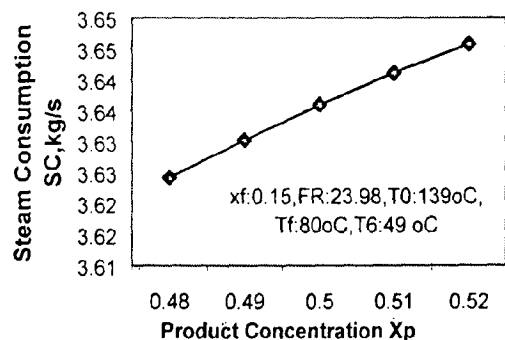


Fig-3.10 Effect of Product Concentration on Steam Consumption

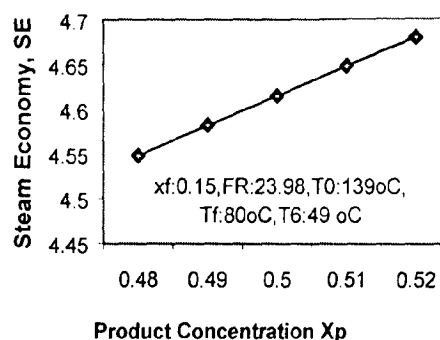


Fig-3.11 Effect of Product Concentration on Steam Economy

The results are summarized in the following Table.

Table-3.10 Effect of product concentration on SC, SE and A.

ΔX_p , %	SC,%	SE, %	A, %
48-52	0.6	2.88	7.42

3.7.5. Variation of Sc, Se and A with Varying Feed Flow Rate of Weak Black Liquor

Feed flow rate of weak black liquor also affects steam consumption, steam economy and area

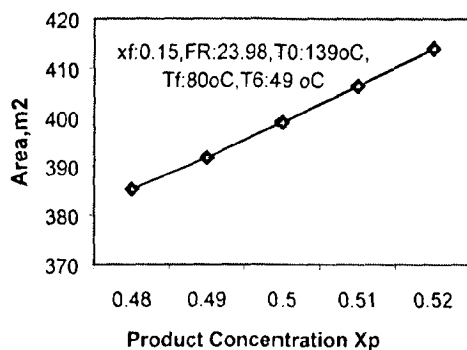


Fig-3.12 Effect of Product Concentration on Area

demand of MEE. Figs. 3.13 –3.15 show their effects when they are varied between 17.98-24.98 kg/s.

These values have been found to be appropriate as it covers the range of black liquor flow from 100 TPD to 300 TPD pulp mill assuming 1.4 kg-2.0 kg black liquor solids per kg of pulp. Assuming 15% inlet concentration for weak black liquor one can find out the flow rates of liquor as shown in the following Table. Higher input concentration will reduce this value but still remain within the range. It is interesting to note that these are the normal values for wood and bamboo based mill in India.

The figures reveal that with the increase of feed flow rate, steam consumption and area increase while steam economy remains almost constant. This is attributed to the higher amount of liquor flow rate which invariably demands greater heating surface and more steam consumption for the same percent evaporation. It is evident from figures that SC and area(A) increases significantly in the order of 38.88% and 38.62% respectively while there is very little change (can be assumed negligible change) in steam economy. For all practical purposes this can be considered constant. This is clearly understandable as with the increase of liquor flow rate more amount of steam is required for proportional increase of vapor production rate; thus the ratio remains practically constant.

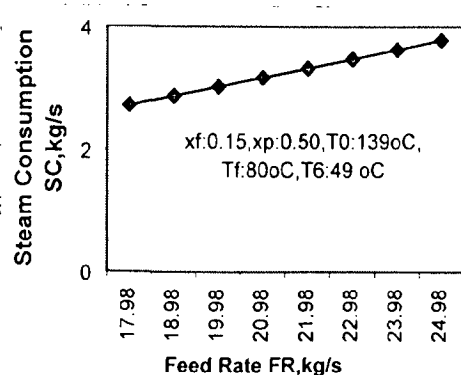


Fig-3.13 Effect of Feed Rate on Steam Consumption

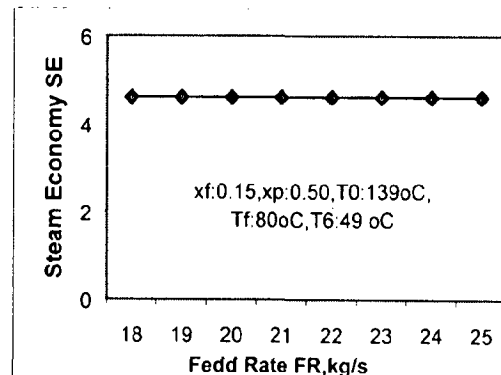


Fig-3.14 Effect of Feed Rate on Steam Economy

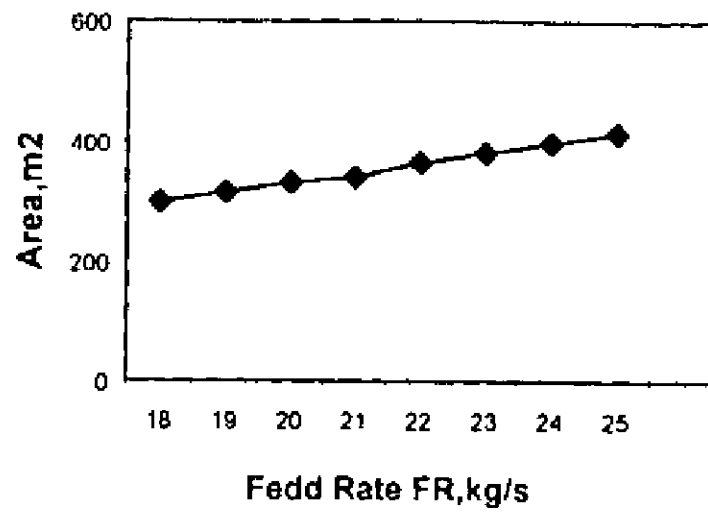


Fig-3.15 Effect of Feed Rate on Steam Consumption

Table- 3.11 Feed flow rate, kg/s for different production rate.

Pulp ,TPD	Black liquor solids, t/t of OD pulp						
	1.4	1.5	1.6	1.7	1.8	1.9	2.0
100	10.80	11.57	12.35	13.12	13.88	14.66	15.43
150	16.2	17.36	18.51	19.67	20.83	22.0	23.15
200	21.6	23.15	24.68	26.23	27.78	29.32	30.86
250	27.0	28.94	30.84	32.78	34.72	36.65	38.58
300	32.41	34.72	37.01	39.34	41.67	43.98	46.30

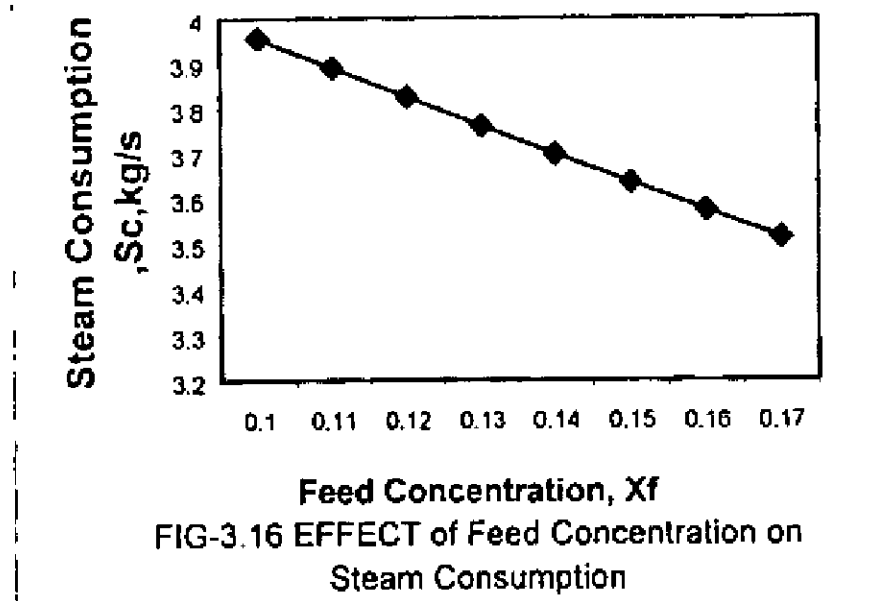
For better clarity the results in brief are shown in the following Table.

Table-3.12 Effect of feed flow rate on SC, SE and A.

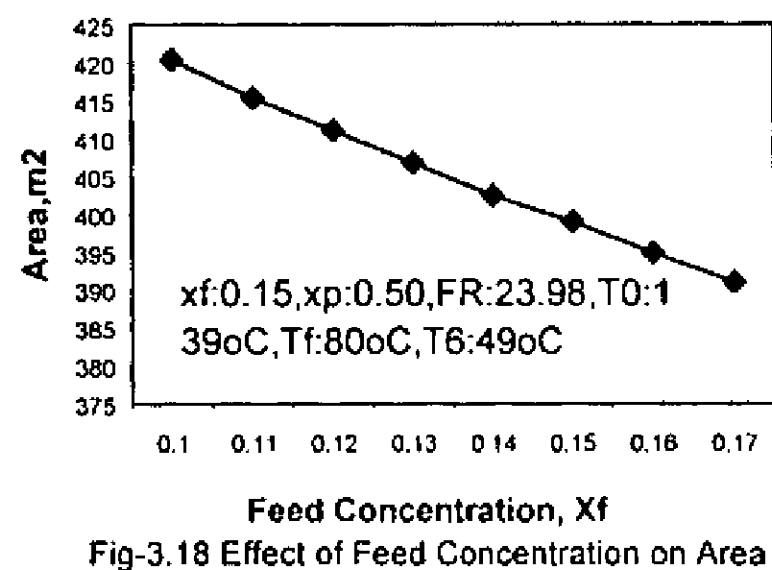
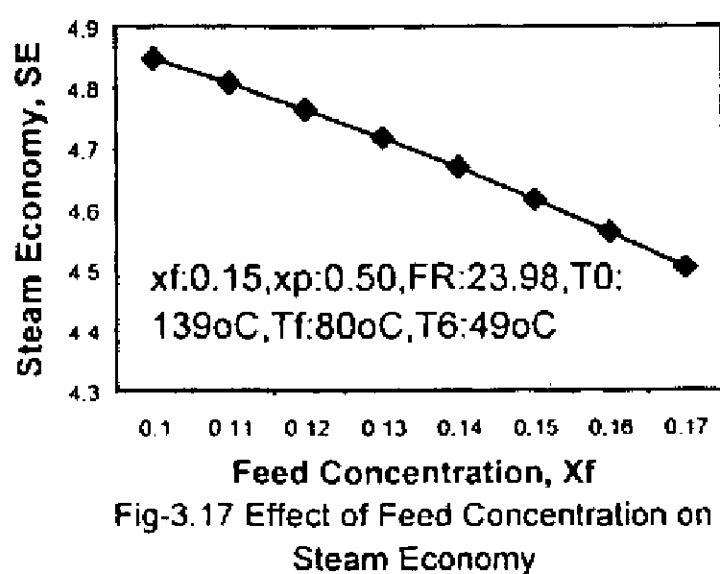
Δ FR, kg/s	SC,%	SE, %	A, %
18-25	38.88	No change	38.62

3.7.6. Influence of Feed Concentration on Steam Consumption(S_c), Steam Economy(S_e), Area Requirement(A)

The total solids concentration of the evaporator feed liquors influences the steam economy and



steam consumption and area requirement for MEE. If the feed solids concentration is raised all the parameters will decrease. This is more clearly shown in Figs. 3.16-3.18. It has been noticed that all parameters namely S_c , S_e and A decrease to the extent of 8.12%, 5.47% and 4.89% respectively with the variation of feed concentration X_F . The steam consumption varies linearly while the steam economy and area varies with slight curvilinear characteristics.



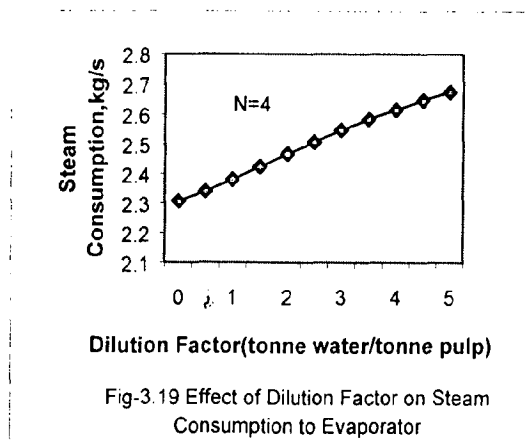
The results are summarized in the following Table.

Table-3.13 Effect of feed concentration on SC, SE and A.

$\Delta X_f, \%$	SC, %	SE, %	A, %
12-17	8.12	5.48	4.89

3.7.7 Interaction of MEE with BSW Operation

Fig. 3.19 shows the effect of dilution factor on steam consumption in evaporator for four washers. Increase in dilution factor results in increased steam consumption. This is an expected behavior. It is attributed to more dilution of black liquor resulting lower feed concentration. Liquor flow rate to evaporator increases with the increase in dilution factor also. To evaporate this extra liquor more steam is required. Nearly 5.6% steam consumption is increased if one intends to increase dilution



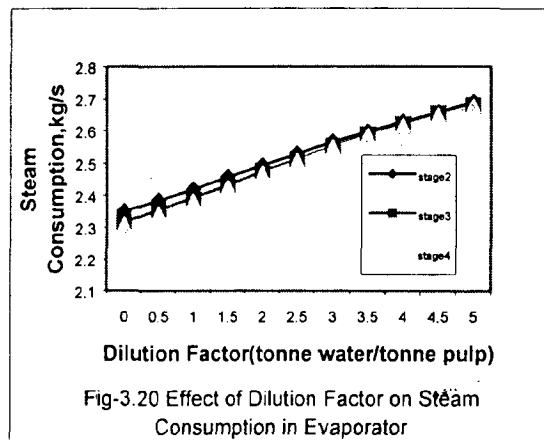
factor from 2.0-4.0 for four stage washers. Although this change is not very high but for economic purpose it has a great influence on total cost of washing on annual basis.

Fig.3.20 shows the effect of dilution factor and number of stages of BSW on steam consumption kg/s. It is evident from the figure that if one goes on increasing dilution factor, steam consumption kg/s will be increased. For a fixed dilution factor steam consumption decreases with the increase of

number of stages. In this study two, three and four stages are considered as they are more prevalent in industries. It is interesting to note that if one increases from 2 stage system to 3 stage system and then from 3 stage system to 4 stage system for a fixed dilution factor (2.5), the relative decrease in steam consumption can be on the order of 0.70% and 0.17% respectively. It is clearly reflected from the data and the figure that though not very much gain is obtained in terms of steam consumption but on the basis of annual consumption it seems to be significant.

3.7.8 Statistical Analysis

A typical set of data is given in Table-2 in APPENDIX-VII which have been made based on the results of Chap-2. For various DF and N, % solids to evaporator is calculated. Using this as concentration, steam consumption is obtained for various DF and N. The data subjected to



statistical regression analysis. For the above Mathcad software is used. The nature of multivariate regression model is nonlinear. The equation is given as

$$Sc = 3.66 \times 10^{-3}(DF \cdot N) + 5.39 \times 10^{-3}(N^2) - 0.054(N) + 2.43 + 0.073(DF) - 2.207 \times 10^{-3}(DF^2),$$

With $R^2 = 0.999$

3.8. CONCLUSION

From the computer program developed on the models and detailed analysis of computed results the following conclusions can be drawn. However the results are shown by varying one parameter out of six (viz., steam temperature, feed temperature, feed concentration, feed flow rate, and last body temperature) while the rest three parameters are kept constant.

- a. With the increase of steam temperature for a fixed set of other operating conditions steam consumption increases, both steam economy and area decrease
- b. With the increase of feed temperature, steam consumption and area decrease while the steam economy increases
- c. With the increase of feed concentration steam consumption, steam economy and area decrease.
- d. With the increase of feed flow rate both steam consumption and area increase but steam economy remains almost constant.
- e. Rising the last body temperature steam consumption decrease but both steam economy and area increase.
- f. With the increase of product concentration steam consumption, steam economy and area increase.

The most advantageous point is to increase the feed temperature. Around 2.1% steam saving is possible at normal working conditions if one increases the feed temperature by 10⁰C. The mathematical models developed and the solution technique employed in this present investigation can precisely evaluate data for any sequence of any MEE set up. The computational procedure developed helps to generate large body of data and can handle many variables and their interactions and interdependence with each other. In today's context it is extremely essential to use this software for the benefit of industry, paper mill in particular. The design procedure developed can bring accuracy in assessing the performance of an existing evaporator system or can help in designing a new system for a Greenfield pulp and paper mill.

Table-3.5 Operational data for MEE

S.No.	Parameters	Values
1.	Liquor feed rate, kg/s	23.98
2.	Liquor feed temp., °C	80
3.	Liquor feed concentration	0.15
4.	Final product concentration	0.50
5.	Steam temp, °C	139
6.	Last body temp., °C	49
7.	Heat transfer area, m ²	400

Table- 3.14 Geometric design parameters of LTV evaporator

Evaporator: Mild Steel Evaporator, Tube: Stainless Steel, Length (L) / Diameter (d)> 80-190

S. No.	Parameters	Values	S. No.	Parameters	Val
1.	Tube size, mm	50.8	5.	Thickness of tube, mm	2.76
2.	No. of Tubes	350	6.	Thickness of tube shell, mm	18
3.	Heat transfer surface, m ²	400	7.	Tube length, m ²	7.2
4.	Pitch(Triangular), mm	70			

CHAPTER-4

MATHEMATICAL MODELING FOR BLEACH PLANT

4.0 INTRODUCTION

As indicated in Chap-1 that ever increasing costs of chemicals, energy and other inputs and legislation of the pollution control authorities for treatment of the generated effluents due to chemical reaction between the reactant and pulp in various stages such as pulping and bleaching has forced the paper Industry to optimize various processes and operations to be effective work in a most economical way. The details of bleaching process and operations are also described in Section 1.3.3 of Chap-1. Bleach plant effluent, in fact, presents the highest pollution load in paper industry compared to any other operation. For an idealized paper mill using bleached Kraft

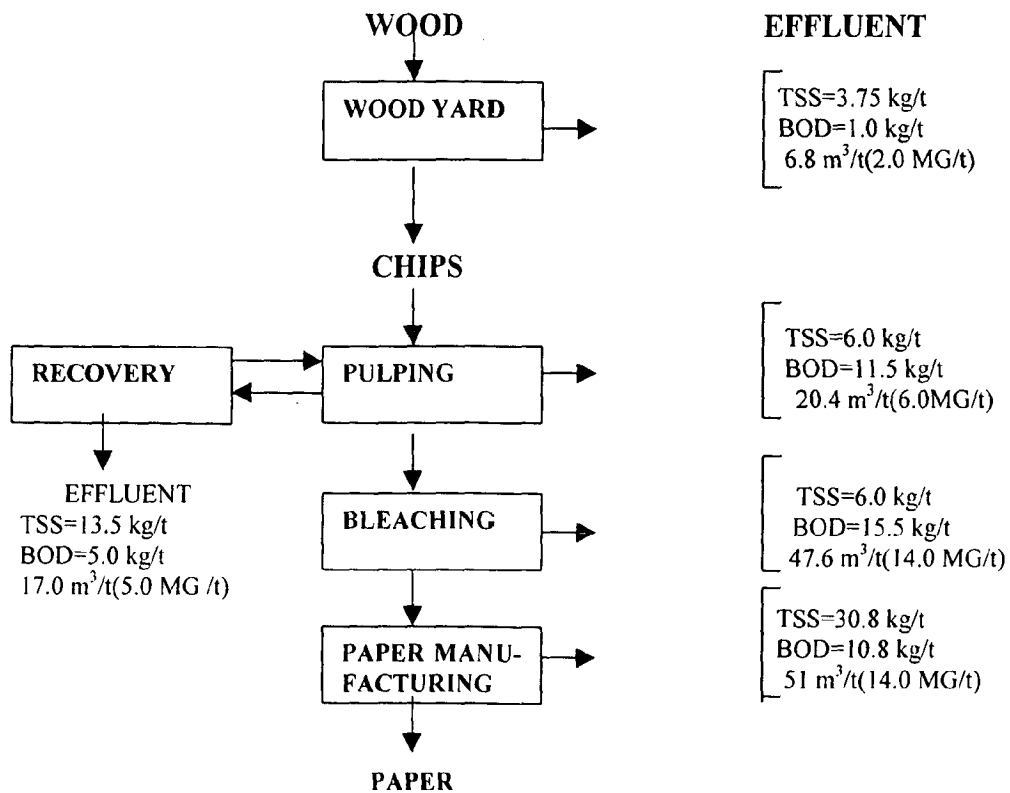


Fig.a Effluent loads of different sections.

pulp, Kumar and Branion(57) has shown the extent of effluent loads of five different sections as shown in the diagram

Demands imposed by both regulatory and market pressures are for new technology to uproot this problem of energy and environmental issues. From detailed survey of most Indian mills and mills abroad(8,18,62,82,115), it is evident that there are large variations observed in case of pollution parameter and energy values; the data are also highly scattered. For sustainable development of this industry, this pollution load has to be reduced to a level to adhere to the stipulated values of the parameters given by pollution control authorities.

Formation of AOX starting from low to high molecular weight compounds in bleach plant effluent considered to be the most toxic, is mainly attributed to consumption of chlorine originating from elemental chlorine and/or chlorine dioxide in bleach plant using chlorine based chemicals. The content of chlorinated organic matter present in the bleach plant varies depending on types of raw material, bleaching chemicals, bleaching conditions, extent of bleaching and the type of chlorine based sequences.

A number of other factors are of importance for the pollution load from the bleach plant e.g. the washing loss of the incoming pulp, the type of lignin and its content of incoming pulp or the kappa number of pulp. Poor brown stock washing affects the chlorine demand in the chlorination stage. A good washing ensure low carry over of dissolved organics into bleach plant and thereby decreases the consumption of bleaching chemicals and the discharge of chlorinated organic matter in the bleach plant effluent. The dissolved organics carried to bleaching stage due to poor washing efficiency, serves as precursor to AOX and other chloro-organic formation.

Bleach plant optimization is one of the steps which can help reduce the consumption of these inputs to minimize pollution load generation in paper mills and to cut down costs for the overall economy in a pulp and paper mill.

There is an urgent need to attend these issues in terms of assembling the reproducible data in a databank and then quantifying them for design estimation. There is also ample scope to develop a model in terms of the interdependency among the various parameters.

This chapter addresses these aspects in three sections:

- Optimization of multistage bleach plant assuming no carry over solids with the pulp using the variable κ –the kappa number of the efficiently washed pulp.
- Development of algorithm to calculate the extra consumption of chemicals due to carry over solids with the pulp from BSW.
- Selection and development of equations to estimate the pollution parameters.
- To assess pollution load entering to the effluent treatment plant(ETP).

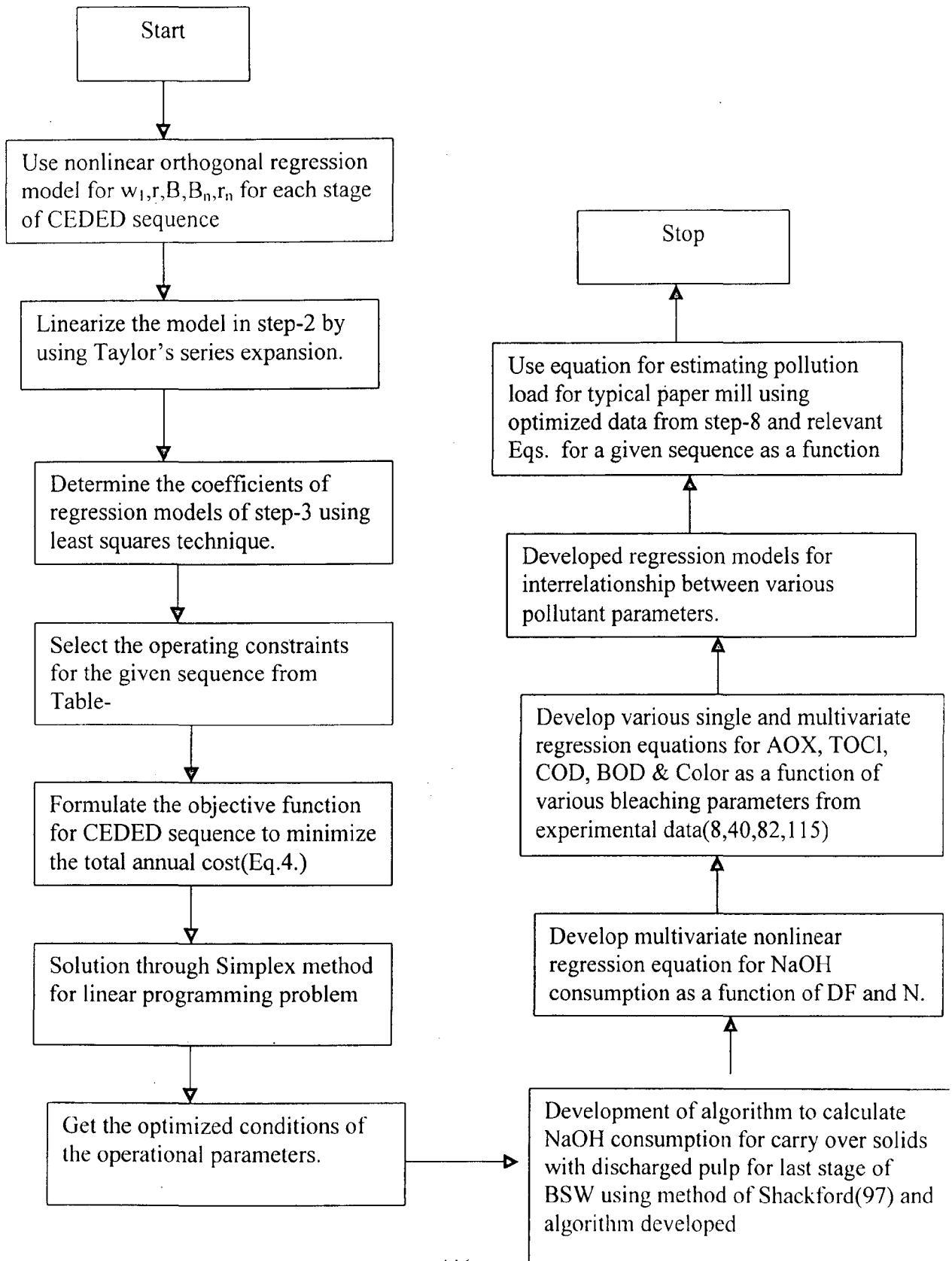
These are discussed in the following paragraphs. For easy understanding a flow chart indicating the sequence of calculation is given.

4.1 BLEACH PLANT OPTIMIZATION

Practically limited attempts have been made for modeling or optimization of bleach plant with a view to improve efficiency vis a vis to reap economic benefits in a paper mill.

Shackford (97) had attempted to present an optimum design and operation to achieve the best results possible for a bleach washer. Unfortunately, this is confined to a segment of a bleach plant and not the whole bleach plant as a whole. Freedman (23) of FOXBORO Company, USA, has developed optimization in a true sense for a specific sequence of a bleach plant using a nonlinear model which is linearized by Taylor series expansion and the coefficients are determined from plant data reported by Moor and Haner(69). Substantial cost benefit of nearly 14.5% due to savings in chemicals and steam has been indicated. No other works are reported to-date to the author's knowledge.

Flow chart for optimization of multistage bleach plant for CEDED is given below:



In this present investigation a bleach plant of identical sequence CEDED has been assumed to examine the applicability of the models presented by them at the first stage as a part of investigation and then extending them to wider range of data of the variables. A typical diagram of CEDED sequence is shown in Fig.b. The functions of each stage is very much clear from diagram. Further, enlarging of the stage(like CEHDED,CEDEDH/P etc.) and using longer sequence(CEH,CEHH etc.) have not been attempted as it is well known that longer the sequence degree of difficulty is more for modeling, optimization and control of the bleach plant. The sequence mentioned above will consume much chemicals, generate more acute toxic compounds to achieve same degree of brightness with drastic shrinkage of pulp or can reduce brightness with same amount of chemicals applied.

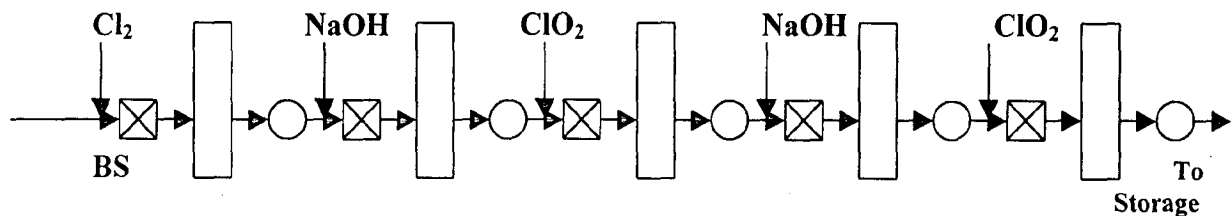


Fig.b A five-stage bleach plant consisting of chlorination, alkaline extraction, chlorine dioxide, alkaline extraction, and chlorine dioxide stages.

To perform bleach plant optimization, one has to select an objective function for minimizing total cost of operation of a bleach plant. The cost of a bleach plant depends primarily on following points:

- Cost of bleaching chemicals which is a function of many variables including wood specific kappa number entering bleach plant, bleach sequence, retention time in towers, the operating temperature in the towers and the conditions of the inter-stage bleach washing and the mixer efficiency in the mixer.

- The operating cost of bleaching is also a function of the degree of removal of the previous stage by-products as well as pH adjustment in the succeeding stages, besides the cost of energy required in pumping, mixing, inter stage washing plus the steam requirement for adjusting the temperature.

For a multistage bleach plant the objectives are usually multi choices like maximum brightness, minimum pollution load generation(BOD,COD,AOX, SS, TDS, TOCl etc.), minimum color reversion(post color number) ,maximum throughput, minimum strength loss and minimum cost etc.

Using Freedman' concept, the last one is taken as the objective function, considered to be a linear function of decision variables (the major cost i.e. chemical cost, steam cost etc.) of the bleach plant, which is to be minimized. The objective function thus can be formulated for a specific target variable (brightness, strength) as follows:

$$Z=C_0+ C_1x_1+ C_2x_3+ C_3x_5+ C_4y_1+ C_5y_3+ C_6y_5$$

The above objective function can be subjected to LP to minimize the cost to get optimal values of the parameters.

4.2 DEVELOPMENT OF MATHEMATICAL MODEL FOR BLEACH PLANT

Model building of multi-stage bleach plant is possible if some logical and systematic approach for understanding the design and analysis of the problem is attempted and if optimization is needed, this can be exercised through economic descriptions of the operations of this system.

The optimization procedure of bleach plant is discussed in the following subsections

4.2.1 Development of Model of Multi-stage Bleach Plant

As already indicated, the bleaching operation is an extremely complicated process which involves a number of variables. It is very difficult to correlate various input to output parameters for any bleach plant, even for a single stage. One can however optimize the bleaching operation by

defining the cost function and constraints for one's own brightness, kappa number, and residual chemical specifications. Some of the cost parameters are strongly dependent on many input parameters. The output parameters depend on pulp type, temperature, consistency, pH, time and initial kappa number. Though large body of data and graphics are available regarding optimization of bleaching, no mathematical treatments are given except the one reported above(23). However, the solution technique has not been shown anywhere.

For a multistage bleach plant like CEDED, one can develop a separate model for each stage but each stage does not have a large effect on the target variables(brightness, strength etc.). Therefore, it is prudent to assume one model to show combined effect of two stages. For the first two stages (CE), Eqs. (4.1) and (4.2) are used. For each succeeding stages (D) and (ED), two general Eqs. (4.3) and (4.4) are employed. These equations describe the effects on kappa number, residual chemicals, brightness of charging chemical, temperature, retention time, and brown stock kappa number. The nonlinear aspects of models in some stages are also considered. The parametric influence on the desired parameter is usually presented by a polynomial of any order to take care of non-linearity. The coefficients are normally evaluated through least square techniques for multiple regression analysis. The details of the techniques are given in APPENDIX-III. Using the above statistical method, the regression equations of Kappa Number(w_1), residual chemicals(r), brightness(B) and brightness for nth stage(B_n), residual chemicals for nth stage (r_n), can be written in nonlinear-orthogonal form, as follows:

$$w_1 = w_{10} + a_1(w_2 - w_{20}) + a_2(w_2 - w_{20})^2 + b_1(x - x_0) + b_2(x - x_0)^2 + c_1(y - y_0) + c_2(y - y_0)^2 + d_1(s - s_0) + d_2(s - s_0)^2 \quad (4.1)$$

$$r = r_0 + a_3(w_2 - w_{20}) + a_4(w_2 - w_{20})^2 + b_3(x - x_0) + b_4(x - x_0)^2 + c_3(y - y_0) + c_4(y - y_0)^2 + d_3(s - s_0) + d_4(s - s_0)^2 \quad (4.2)$$

$$B_n = B_{n0} + e_1 \Delta w_{10} + e_2 (\Delta w_{10})^2 + f_1 \Delta x_0 + f_2 (\Delta x_0)^2 + g_1 \Delta y_0 + g_2 (\Delta y_0)^2 + h_1 (\Delta s_0) + h_2 (\Delta s_0)^2 + j_1 \Delta u_0 + j_2 (\Delta u_0)^2 \quad (4.3)$$

$$r_n = r_{n0} + e_3 \Delta w_{10} + e_4 (\Delta w_{10})^2 + f_3 \Delta x_0 + f_4 (\Delta x_0)^2 + g_3 \Delta y_0 + g_4 (\Delta y_0)^2 + h_3 (\Delta s_0) + h_4 (\Delta s_0)^2 + j_1 \Delta u_0 + j_2 (\Delta u_0)^2 \quad (4.4)$$

4.2.2 Linearization of the Models

It is imperative to linearize a non linear model by a series expansion either Maclaurin's or Taylor's series expansion for further analysis. In this work, the nonlinear model equations are linearized by a general Taylor's series expansion and neglecting the higher order terms, the following equations yield:

$$w_1 = w_{10} + a\Delta w_{20} + b\Delta x + c\Delta y + d\Delta s \quad (4.5)$$

$$r = r_0 + a\Delta w_{20} + b\Delta x + c\Delta y + d\Delta s \quad (4.6)$$

$$B_n = B_{n0} + e\Delta w_{10} + f\Delta x + g\Delta y + h\Delta s + j\Delta u \quad (4.7)$$

$$r_n = r_{n0} + e\Delta w_{10} + f\Delta x + g\Delta y + h\Delta s + j\Delta u \quad (4.8)$$

where $\Delta x = x - x_0$

If a variable does not have a large effect, the variable would be dropped from the model for that particular stage.

4.2.3 Determination of Coefficients

For each plant, there is a range of parameters in which the model is valid. For different set of ranges of parameters, one has to calculate new coefficients. In Eq. 4.1, extracted kappa number is a function of temperature, chemical used, and retention time in chlorination stage. By drawing a curve (it may or may not be nonlinear) and projecting the straight line on this operating curve from reference point to the current operating point gives the range of parameters within which the linearization is valid

In this present investigation, functional relationship for each variable has been developed by Multiple Regression analysis using the software named MATHCAD. The data reported in Singh(99) are employed for regression equations Eq.4.11 and 4.13 and data of Histed and Janovas(41) are also used for regression equation, Eq.4.9 to determine the coefficients.

4.2.4 Selection of the Operating Constraints

It is well known that a model can be valid or accurate if it contains all the objectives, constraints and decision variables relevant to the problem or actually part of the problem.

The operating conditions are used as constraints because each plant has a limit for an operating variable. For example, each sequence has a limit of chemicals used, temperature, retention time etc. in a particular stage. These limits are put in the form of mathematical inequalities. These are then used as constraints for the LP. If we use large amount of chemicals, and high temperature will cause the accelerated color reversion or poor strength, higher pollution load and more energy consumption. Minimum time for completion of the reaction to get desired value of brightness is also needed for each stage. Therefore, it is important to use the set of constraints (operating variables) properly. These constraints can be exemplified for stages (combined or single as a case may be) as:

$$\begin{array}{lll} x_1 \geq 60 \text{ kg/tonne of pulp} & s_1 \geq 120 \text{ min} & y_1 \geq 40 \text{ }^\circ\text{C} \\ x_2 \geq 8 \text{ kg/tonne of pulp} & s_2 \geq 180 \text{ min} & y_2 \geq 60 \text{ }^\circ\text{C} \\ x_3 \geq 6 \text{ kg/tonne of pulp} & s_3 \geq 120 \text{ min} & y_3 \geq 70 \text{ }^\circ\text{C} \end{array}$$

4.2.5 Solution Through Linear Programming Technique

The process of solving an LP requires a large number of calculations and is therefore performed by a computer program. In the present work, the computer software package known as LINDO can be used. The main purpose of LINDO is to quickly input an LP formulation, solve it, assess the correctness or appropriateness of the formulation based on the solution, and then quickly make minor modifications to the formulation and repeat the process. To solve the LP problem, LINDO requires operating data of various stages of CEDED bleach plant. The operational data presented by Freedman are used to check their validity. It agrees excellently without

noticeable error. In this work, the operating data due to Sklarewitz and Parker (101) given in Table- 4.1 are used as initial conditions.

4.2.6 Operating Data for Simulation

It is very difficult to estimate the cost of individual chemicals used for industrial usage as it varies not only with the purity of product but also with the market trends for escalation of cost indices. However it is fairly accurate to assume the constant ratio of costs of bleaching chemicals which are available elsewhere. The ratio of the costs of the chemicals reported by various investigators is depicted in Table-4.2

Table-4.1 Typical and calculated operating data for a CEDED bleachery

Stage	T, °C		Cy, %		Ce,%		t		pH	
	a	b	a	b	a	b	a	b	a	b
C	20	20	3-4	3.78	5-7	6.64	40 min	40 min	<3	2.6
E	70	70	12-14	11.9	3-4	3.66	2 hr	2 hr	11	11.99
D	70	70	12-14	13.9	0.6-1.0	0.75	3 hr	3 hr	3.5	4.8
E	70	70	12-14	14.0	0.5	0.47	2 hr	2 hr	-4	9.3
D	70	70	12-14	14.0	0.3-0.5	0.32	3 hr	3 hr	11	8.8
									5-6	

** T=Temperature, Cy= Consistency, Ce= Bleach chemical charge, t=Time, pH= Final pH

a=Typical, b=calculated

In this present work ,however the ratio of cost of chemicals(Cl_2 :NaOH:NaOCl:ClO₂) can be taken as 1:1.3:2.14:5.72. Using this ratio, it is easy to find out the cost of other chemicals if one of them is known. Using an average ratio of costs of bleaching chemicals (23,39) and taking the cost of chlorine from Jim Haynes et al.(39) other chemicals costs are calculated.

Table-4.2 Ratio of the cost of chemicals

Reference	Chemicals	Ratio
(2)	Cl ₂ : NaOH:NaOCl:ClO ₂ :	1:1:2.15:5.72
(9)	Cl ₂ :NaOH	1:1.3
(12,17)	O ₂ :H ₂ SO ₄ :NaOH:MgSO ₄ :ClO ₂ (as active Cl ₂):H ₂ O ₂ :O ₃ :Chelating agents	1:1.14:3.14:5.29:6.14:12.57:17.14:21.42
(13)	O ₂ :NaOH:Cl ₂ :ClO ₂	1:1.375:1.375:2.5
(14)	O ₂ :MgSO ₄ : NaOH:Cl ₂ :ClO ₂ (as active Cl ₂):	1:1.2:1.4:1.25:2.5
(15)	O ₂ :HOCl:ClO ₂ :H ₂ O ₂	1:4:9:12
(16)	Silicate 41 ⁰ Be:SO ₂ :NaOH:Na ₅ DTPA:Na ₂ S ₂ O ₄ :H ₂ O ₂	1:1.57:1.72:7.29:8.86:9.14

Table-4.3 Cost of bleaching chemicals

Chemical used	Price per chemical, Rs/kg
Chlorine	6.48
Sodium Hydroxide	8.33
Sodium Hypochlorite	13.88
Chlorine Dioxide	37.03
Steam cost(⁰ GE88-90)	0.500

The above unit costs given in Table-4.3 are typically used to formulate the objective function.

4.2.7 Validity of the Models

As indicated, there is no details of analysis published by any investigators. The optimization scheme in this present work has been attempted with the experimental data of Moore and Ha and cost data reported by Freedman. The computed results agree very well without any error. The present model developed on the guidelines by Freedman (23) is found to be most appropriate and efficient one that can be used to any bleach plant

4.2.8 Calculation Procedure for the Present Sequence

After model validation, one can now proceed for calculation for a specific case as follows:

To describe the optimization procedure for CEDED bleach plant, the derived models for first two stages can be written as:

$$w_1 = a_0 + a_1 \Delta w_{20} + a_2 \Delta x_1 + a_3 \Delta y_1 + a_4 \Delta s_1 \quad (4.9)$$

$$r = r_0 + a_5 \Delta w_{20} + a_6 \Delta x_1 + a_7 \Delta y_1 + a_8 \Delta s_1 \quad (4.10)$$

The model for third stage (chlorine dioxide) is as follows.

$$B_3 = B_{30} + b_1 \Delta w_1 + b_2 \Delta x_3 + b_3 \Delta y_3 + b_4 \Delta s_3 \quad (4.11)$$

$$r_3 = r_{30} + b_5 \Delta w_1 + b_6 \Delta x_3 + b_7 \Delta y_3 + b_8 \Delta s_3 \quad (4.12)$$

The model for fourth and fifth stage (extraction, chlorine dioxide) is

$$B_5 = c_0 + c_1 \Delta B_3 + c_2 \Delta x_5 + c_3 \Delta y_5 + c_4 \Delta s_5 \quad (4.13)$$

$$r_5 = r_{50} + c_5 \Delta B_3 + c_6 \Delta x_5 + c_7 \Delta y_5 + c_8 \Delta s_5 \quad (4.14)$$

It should be noted that the pH dependence is not included in this model as it is not very sensitive parameter and does not give accurate predictions through small changes in H^+ ions. In general, the model can be expressed as:

$$\begin{bmatrix} \Delta B_1 \\ \Delta B_2 \\ \Delta B_3 \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} & a_{16} \\ a_{21} & a_{22} & a_{23} & a_{24} & a_{25} & a_{26} \end{bmatrix} \begin{bmatrix} \Delta X_1 \\ \Delta X_2 \\ \Delta X_3 \\ \Delta X_4 \\ \Delta X_5 \end{bmatrix}$$

To make the calculation easy the equations for extracted kappa number from 1st stage (Eq.4.9), brightness from stage 3rd and 5th (Eqs.4.11 and 4.13) of bleach plant model are used. Using the coefficient calculated, the model Eqs. 4.9, 4.11 and 4.13 can be expressed as

$$w_1 = 7.672 + 0.07 * w_2 - 0.068 * x_1 - 0.014 * y_1 - 0.011 * s_1 \quad (4.15)$$

$$B_3 = 1.977 - 1.118 * w_1 + 11.86 * x_3 + 0.54 * y_3 + 0.019 * s_3 \quad ($$

$$B_5 = 1.633 + 0.276 * B_3 + 9.797 * x_5 + 0.038 * y_5 + 0.003296 * s_5 \quad ($$

In stages IVth and Vth (D & ED stages) cost of relative amount of chemicals used is considered. Using the coefficient for the conversion of stage temperature to steam costs and using price of bleach chemical, the objective function can be expressed as:

$$Z = -148.14 + 6.48 * x_1 + 37.03 * x_3 + 17.89 * x_5 + 10.08 * y_1 + 1.08 * y_3 + 2.16 * y_5$$

The objective function when subjected to the constraints (Eqs.4.15,4.16 and 4.17) gives optimum conditions, presented in Table-2 in APPENDIX-VIII. If one desires to change brightness values, the optimum conditions obtained are shown in Tables-3,4,5 in APPENDIX-VIII.

For final stage brightness 90.88 °GE, using the current operating conditions given in Table- 4.1 and the optimum conditions in Table-2 in APPENDIX-VIII, the total cost involved and the benefits accrued is shown in Table-4.4 which shows a decrease in bleaching cost to the tune of 300/Tonne. By changing the current operating conditions within the given range there is a change in final stage brightness for fixed saving of annual cost. This in turn should affect bleached pulp quality. In each case, the initial conditions of the bleach plant are again taken from Table- 4.1. Using these values as current operating conditions, the cost of producing bleached pulp of different brightness can be on the order of 1200 Rs/tonne.

Table-4.4 Comparison of total cost before and after optimization

Total Cost, Rs per Tonne of Pulp		Total savings	
Before optimization	After optimization	Percentage	Rs per Tonne
1502 (35.76\$)	1200 (28.57 \$)	20.0	300

By using the above optimization scheme can boost the significant economy by saving chemicals and energy in a bleach plant.

4.3 DEVELOPMENT OF MATHEMATICAL MODELS FOR EFFLUENT PARAMETERS

Development of models for estimating the pollution load generation in bleach plant are necessary as it will be extremely helpful in designing an effluent treatment plant(ETP). The cost of treatment can easily be accounted if the values are known. The extra cost due to carry-over solids and fluctuation of kappa number of pulp over a standard values can be ascertained. This value, in fact, is required in optimization of BSW operation. The cost can be expressed in terms of removal of any effluent parameters like BOD,COD,AOX etc. assuming proportional decrease of other parameters.

Before the attempt of model development it is customary to review the status of modeling of effluent parameters. These are given below:

4.3.1 Review of Mathematical Models

There are few model equations available for estimating effluent characteristics in a bleach plant of a paper industry. A bulk of them relates to estimation of AOX, and others are for COD, TOCl, Total Polychlorinated Phenolics(TPP),Chloroform, and Methanol. These models are mostly applicable to softwood(SW) fibres. These are described below:

4.3.1.1 Model Equations for Estimation of AOX

There are three type of model equations available in literature. The first one relates to all input variables and is empirical in nature; the second is a second order parabolic regression equation while the third are mostly used as a mathematically linear equations. The input parameters are varying significantly from investigator to investigator. These are expressed in terms of atomic chlorine or active chlorine, molecular chlorine, percent chlorine –di-oxide, Kappa Factor ,Kappa Number, degree of substitution(SD) etc.

A comparison of all the earlier predicted models is possible when all the models are put in standard form. Because of diversity of parameters and varying mode of expressions the standard form will also be of three types. These are shown in Table-6 in APPENDIX- VIII.

AOX formation has been shown to be directly proportional to the amount of elemental chlorine consumed in the C stage, regardless of the form (Cl_2 or ClO_2). Earl and Reeve (18) have reported the following relationship for estimating the amount of AOX (kg/t) formed in the C stage of a given sequence for Cl_2 and ClO_2 (chemical/t).

$$\text{AOX} = 0.10(\text{Cl}_2 + 0.526 \text{ClO}_2)^2 \quad (4.1)$$

4.3.1.2 Model Equations for Estimation of TOCl

A linear relationship among the amount of Cl_2 , hypochlorite and ClO_2 added and the amount TOCl formed (62) is given by the Eq.4.19.

$$\text{TOCl} = k[\text{ACl}_2 + \text{AClO}^- / 2 + \text{AClO}_2 / 5] ; \quad (4.1)$$

The values of k (constant for a given pulp) are shown in the following Table:

Table-4.5 Equations for estimating TOCl

Eqs.	K(Constant)	Pulp Type	Remarks
1	0.07-0.08	Kraft pulp	Laboratory scale
2	0.1	Kraft pulp	Minimum at mill scale
3	0.14	Kraft pulp	Maximum at mill scale
4	0.074	Pulp pretreated with NO_2	Laboratory scale
5	0.105	Conventional O_2 bleached pulp	Mill scale

Regarding the relationship between AOX and TOCl, the Eq. 4.20 is frequently used in mill practices.

$$\text{AOX} = 1.2 - 2.0 * \text{TOCl}$$

(4.20)

Basta et al.(8) has estimated AOX from experimental data as 1.33 times of TOCl.

4.3.1.3 Model Equations for Estimation of COD, Color, Polychlorinated Phenolics and Chloroform

Like AOX, the COD, color etc. are also expressed differently by different investigators. The reported models are depicted in uniform format as follows.

Table- 4.6 Equations for estimating COD and Color

COD(kg/tonne) = k₁(KF) + k₂(Kappa)+k₃(carry over) +k₄, where KF=kappa factor						
S.No	k ₁	k ₂	k ₃	K ₄	References	Remarks
1.	84.05	2.09	0.0	-12.75	(115)	R ² =0.95 southern pine pulp; kappa No. 31,13 and 14; (DC)E _{op} sequence
2.	0.0	2.4	0.61		(62)	Oxygen delignified (softwood)pulp; kappa number 17.7;bleachingsequence (C50+D50)(EO)D
Color(kg/tonne) = k₁(KF) + k₂(Kappa)+k₃(COD) +k₄						
3.	111.8 5	3.347	0.0	-18.77	(115)	R ² =0.84
4.	0.0	0.0	1.538	1.27	(115)	R ² =0.84
Total polychlorinated phenolics,ppb=k₁(% Cl₂)²+k₂						
5.	35.7	1.89	0.0	0.0	(115)	R ² =0.88
CHCl₃,kg/admt of pulp= K(k₁+k₂ H^{k₃} +k₄R) Where K = kappa number(entering H stage,H = hypochlorite charge(kg active chlorine/ admt of pulp , R = hypochlorite residual (kg/admt of pulp).						
6.	-.023	.0247	0.5	.00823		-

4.3.2 MODIFICATION OF EXISTING MODEL

It is evident from the review that there are many variations in the data predicted from model. However, some models even deviate from the experimental data from which constructed. These might be due to different sequences used by the different investigators. B models can be formulated for more accurate predictions. An attempt has been made in this section to develop the same. The regression equation are however exercised for AOX, COD and Color. In order to develop the model the same set of experimental data employed by previous investigators (8,115) has to be used. Otherwise models can not be compared.

In this study, the statistical technique for single and multi-variate nonlinear regressions adopted. The algorithm of various statistical techniques are depicted in APPENDIX-VI. MATHCAD software is employed to develop the same.

4.3.2.1 Statistical Regression Equation for AOX

Based on the data of Basta (8) et al. the following multivariable nonlinear regression equation function of CF (Chlorine factor), %D (%Chlorine di oxide substitution).

is obtained. The details of the conditions are given in Table-6 in APPENDIX-VIII.

$$\text{AOX} = -0.218 + 0.01(\%D) + 2.065(\text{CF}) - 8.714\text{E}-05(\%D)^2 - 0.017(\text{CF} * \%D) + 8.0\text{E}-03(\text{CF})^2; R^2 = 1 \quad (4.1)$$

4.3.2.2 Statistical Regression Equation for COD

Tsai (115) et al. obtained a multivariable linear regression equation for COD. The same data is used in this investigation to obtain another multivariable nonlinear regression equation as follows:

$$\text{COD} = -159.526 - 0.354(\text{kappa})^2 - 569.556(\text{KF})^2 + 3.345(\text{KF} * \text{kappa}) + 17.408(\text{kappa}) + 161.727(\text{KF}); R^2 = 0.976 \quad (4.2)$$

4.3.2.3 Statistical Regression Equation for Color

Using the data given by Tsai (115) et al. the following polynomial regression is as follows:

$$\text{Color}=283.745+0.732(\text{kappa})^2-1.75*10^3(\text{KF})^2+7.875(\text{KF}*\text{kappa})-30.164(\text{kappa})+397.041(\text{KF});$$

$$R^2=0.907 \quad (4.23)$$

$$\text{Color}=45.296+.027(\text{COD})^2-0.89(\text{COD}); R^2=0.886 \quad (4.24)$$

It is clear that the two equations are related to different parameters, either kappa number and KF or COD.

4.3.3 Development of Interrelationship between Various Pollution Parameters

Development of inter-relationship among various parameters is important to estimate one (e.g BOD) from the other(e.g. COD). Attempt has been made to develop some of them as follows:

4.3.3.1 Relationship between BOD and COD

There is no regression equation available in literature to estimate BOD. However, Heimburger et al.(40) presented a detailed account of experimental data of BOD and COD for various sequences and also for both SW and hardwood(HW). The range for COD and BOD lie 101 –19 and 31-3 respectively. The lower values are valid for non chlorine bleaching sequences. It has also been found earlier that COD increases with increase of kappa number, increase of carry over solids and in turn with the increase of BOD values. In this present work the following regression equations for BOD are developed to get an order of estimate values:

- **Softwood(Brightness 90%,Kraft unbleached kappa No. 30.6-32)**

$$\text{BOD} = -2.597 + 0.32(\text{COD}) ; R^2=0.816 \quad (4.25)$$

- **Hardwood(Brightness 90%,Kraft unbleached kappa No.15.8-16)**

$$\text{BOD}=0.313+0.172(\text{COD});R^2=0.406 \quad (4.26)$$

- **Combined data of Hardwood and Softwood (linear and nonlinear)**

$$\text{BOD}=-3.432 + 0.323(\text{COD}); R^2=0.862 \quad (4.27)$$

$$\text{BOD}=-0.275+0.184(\text{COD})+1.187*10^{-3}(\text{COD})^2; R^2=0.871 \quad (4.28)$$

It is interesting to note the following observations:

(a) Correlation of BOD with COD is extremely poor for HW; moderate for SW but combined (irrespective of species, kappa No. and sequence) data give better correlation in both linear and nonlinear forms though nonlinear gives slightly superior results.

(b) Approximately COD is found on the order of 2.2 – 4 (mostly 3-4) times of BOD over the entire range of values.

(c) Within the range of values of BOD (11-31 kg/t) in bleach plant applicable for CE/DEI sequence, the correlation fits the data close to almost 100%.

Though BOD and COD relationship is always complex, this preliminary investigation can throw some light on these aspects.

4.3.3.2 Relationship between Kappa Number and BOD (For CE stage)

BOD is linearly dependent on kappa number of the pulp. The data of Raghuvver (82) are used for development of regression. On closer scrutiny of data it is evident that the BOD can be correlated with kappa number in C+E stage.

Using the experimental data (82) for bamboo pulp, the following regression equations are also obtained:

(a) Linear regression:

$$\text{BOD}_5 = 12.648 + 0.192(\text{kappa}); R^2 = 0.974 \quad (4.29)$$

(b) Polynomial regression:

$$\text{BOD}_5 = 9.314 + 0.416(\text{kappa}) - 3.612 \times 10^{-3}(\text{kappa})^2; R^2 = 0.983 \quad (4.30)$$

It is noteworthy that both linear and nonlinear correlations are good though through the nonlinear model equations, one can achieve better accuracy.

These regression equations are valid within the range of kappa number between 22-40 (Bamboo Pulp). The models possess the limitation of not having soda loss as a parameter.

4.3.3.3 Relation between BOD and Soda loss

The data (82) shows that with the increase in washing loss, BOD increases. A relationship is obtained between BOD and washing loss as follows:

(a) **Linear regression:**

$$\text{BOD}_5 = 3.167 + 0.386(\text{SL}); R^2 = 0.974 \quad (4.31)$$

(b) **Polynomial regression:**

$$\text{BOD}_5 = 3.45 + 0.343(\text{SL}) + 1.214 \cdot 10^{-3}(\text{SL})^2; R^2 = 0.984 \quad (4.32)$$

where SL= soda loss

These regression equations are valid for washing loss (Bamboo pulp) 5-10 kg $\text{Na}_2\text{SO}_4/\text{t}$ in chlorination stage. It is reflected that linear regression gives nearly the same reproducibility. The equations, however, suffer from the limitation that it does not contain kappa number values. BOD as a function of both soda loss and kappa number could not be established as no experimental data in this regard are available.

4.3.4 Statistical Interpretation of Models

The experimental data of (8,115) for AOX, COD, color ,BOD, TOCl etc. are compared shown in APPENDIX-VIII. Further interpretations statistically are made through graphical plots between predicted vs actual values (experimental). Residual plots between residuals and predicted values are also attempted.

Figs. 4.1 through 4.7 represent the comparison for AOX(Eq.4.21),COD(Eq.4.22),color(Eq.4.23),

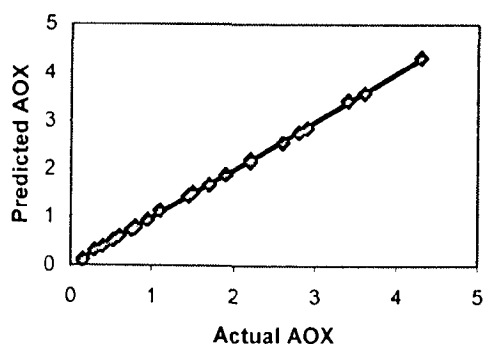


Fig. 4.1 Actual AOX vs Predicted AOX

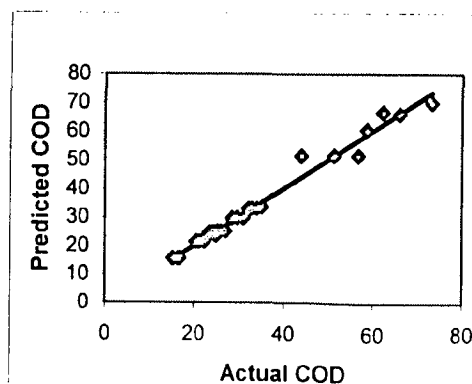
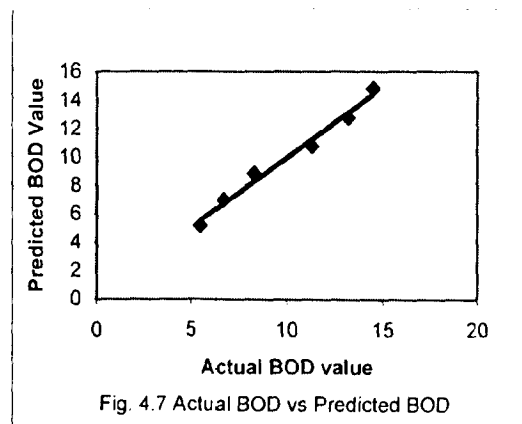
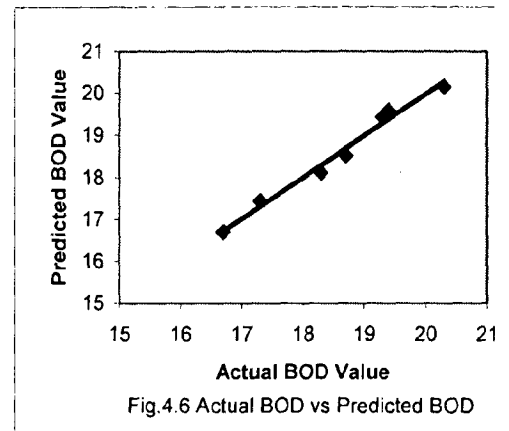
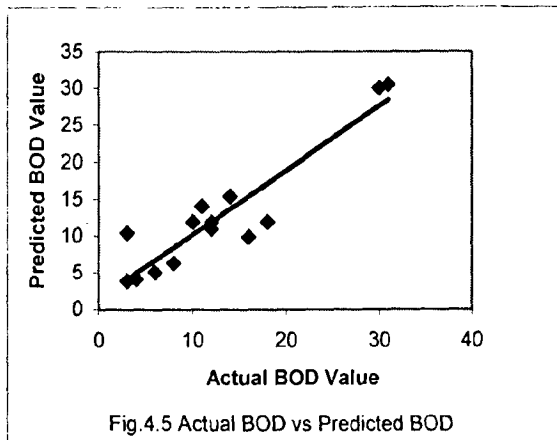
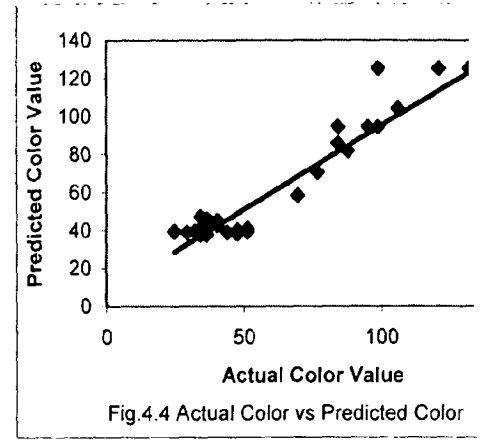
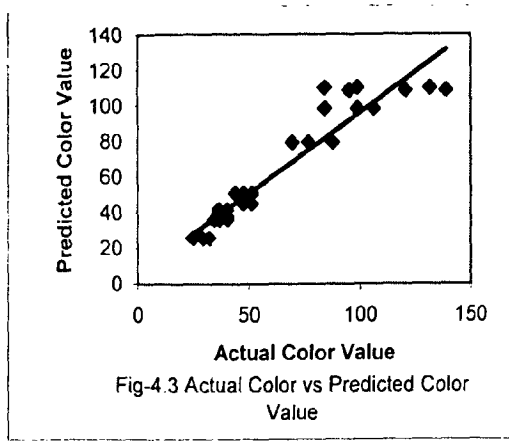


Fig. 4.2 Actual COD Vs. Predicted COD

color(Eq.4.24) ,BOD(Eq.4.28), BOD(Eq.4.30) , BOD(Eq.4.32) respectively. It is evident from the plots that the predicted vs experimental value agree to a high degree of accuracy.



Figs. 4.8 through 4.14 have been drawn to examine the behavior of the residuals as a function of predicted values of the above mentioned parameters. It is clear from the figures that the residuals are almost distributed around zero. The best prediction is obtained for AOX in all cases, then COD will follow. Though the residuals for Color and BOD are not upto the level of accuracy of that for AOX, but still can be accepted for order of estimates, permitted by engineering calculations.

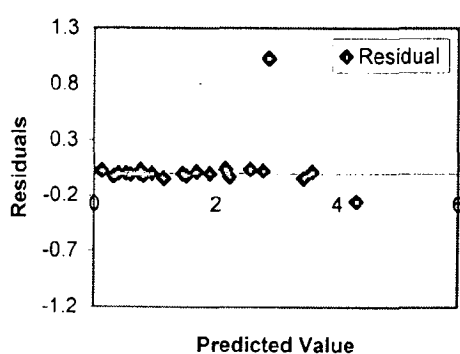


Fig. 4.8 Residuals vs Predicted Value of AOX

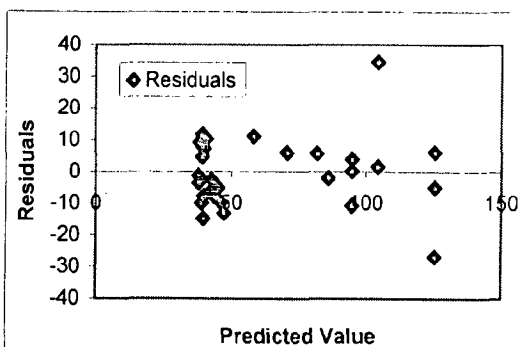


Fig.4.9 Residuals vs Predicted Value of Color

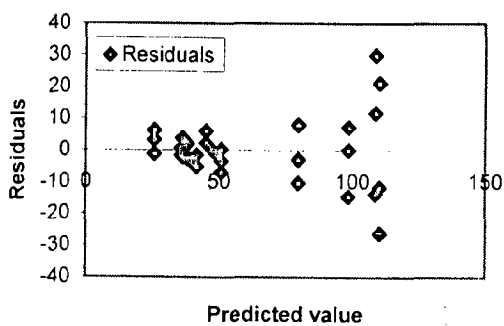


Fig. 4.10 Residuals vs Predicted Value of Color

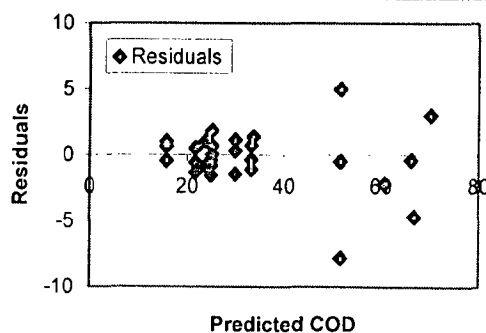


Fig.4.11 Residuals vs Predicted Value of COD

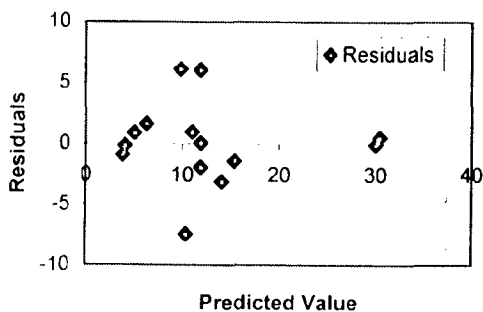


Fig.4 12 Residuals vs Predicted Value of BOD

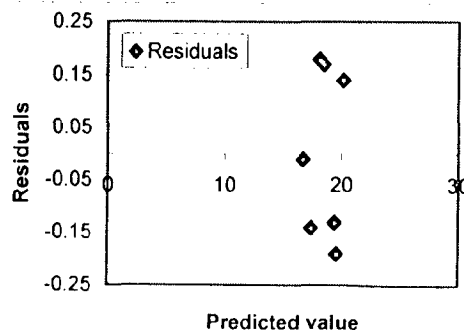


Fig.4.13 Residuals Vs Predicted Value of BOD

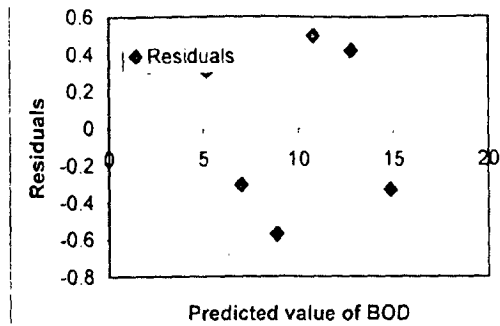


Fig. 4.14 Residuals vs Predicted Value of BOD

Among the BOD residuals, Fig. 4.14 (for soda loss) gives the best prediction. Between t residuals plot for color, the Fig. 4.9(Eq.23) gives better prediction.

It is evident from the data and the graphs that the present correlation for AOX are far superior terms of percentage error, and R^2 values. However, the developed model is valid for CF= 0.5-2 and %D =20-100. In this range of CF and %D ,the percentage error is least as is evident from t Tables-7 and 8 of APPENDIX-VIII. The predicted data from the present model for COD al agrees very well with the experimental data and also much superior to the values through th model predicted by (26) for low as well as for high kappa number values . As stressed upc earlier, these models are helpful in estimating the pollution load entering in to an ETP plant. Once these are accurately known for a particular configuration of bleach plant, the approximate cost c treatment can be ascertained. The methodology for prediction of effluent load is as follows:

4.4 PREDICTION OF POLLUTION LOAD ENTERING TO ETP

The effluent load entering to ETP can be assessed through any of the pollution parameter provided the model equations are precise. Till now no attempt has been made to use any model to estimate the same. Main reason is the uncertainty of obtaining an accurate model developed basec on reliable experimental data. In this present investigation, an order of estimate is made through the models of both AOX, and COD.

4.4.1 Estimation of AOX from Optimized Conditions

For AOX determination, all the models (APPENDIX-VIII in Table-6) reported and also the present one (Eq.4.21) are based on the experimental data for oxygen pre-delignified SW (pine) pulp. The data for HW and bamboo are extremely sparse and scanty. Besides, the experiments conducted on these species are based on limited number of sets with no replica. The accuracy of the data may not be reproducible in actual practice. In this present situation for CEDED sequence, the Eq.2 of Table-6 of APPENDIX-VIII is used. As the source of AOX is only from bleach plant, the predicted data can be directly employed for cost estimates in ETP if one knows the optimized conditions of bleaching of well washed pulp and the distribution of chlorine based chemicals in the sequence.

In the present investigation, the optimum conditions of CEDED sequence (Table-2 of APPENDIX-VIII) has been found out by considering stage 1 (coupling C+E stage) and stage 2 for D only and stage 3 (coupling E+D). The actual distribution is made based on Macdonald(64). The estimated AOX will be on the order of 5.84 kg/t. This equation is however related to softwood only and does not take care of carry over solids. It also does not link with washing parameters. It can be used only for comparison purposes.

4.4.2 Estimation of BOD and COD

On the other hand, for either BOD and COD, the total sum from all sources has to be accounted for. Unfortunately, no correlation of BOD as a function of input parameters for any subsection including bleach plant is available. As earlier mentioned, the developed Eqs. 4.30-4.32 relate either to soda loss or kappa number. On the contrary, the models for COD are not limited. Unfortunately, even for COD, only one equation (Eq.2, Table- 4.6.) due to Lindstrom and Norden(62) connects both kappa number and carry over solids.

A bleach plant has been designed based on certain variables experimentally evaluated on brown stock pulp which invariably contains some minimum amount of unwashable solids (carry over solids) due to adsorption of solutes on pulp fibers as brown stock, absolutely free from BLS is possible. Kokurek(51) and McDonald (64) reported the value in terms of total solids on the order 13.89 kg/t (7.98 kg/t as Na₂ SO₄). Our optimized conditions of bleach plant is based on theoretical assumption of devoid of carry over solids. Chemical consumption due to this minimum amount has to be incorporated. Therefore, the above optimization procedure requires some minor correction to use in ETP. More accurate prediction of carry over solids in a fully washed bleach plant needs detailed modeling of adsorption- desorption kinetics of all adsorbates (lignin, sodium ion and others) and adsorbent (type of pulp). However, for present order of estimate calculation the above will suffice the requirements.

4.4.3 Model Equations for Additional Loads

The equation for COD proposed by Lindstrom et al. can be used for greenfield mill. The mill already having ETP plant should consider the issue of the impact of effluent load over and above the minimum carry over solids and difference of kappa number from floor kappa value of the brown stock. Assuming the value of minimum carry over solids as mentioned above to be constant factor for all DF and N values, the Eq.2 of Table-4.6 for additional loads can be rewritten as :

$$\text{COD} = 2.4 * \Delta \text{Kappa Number} + 0.61(\Delta \text{Carry over solids}) \quad (4.33)$$

Where $\Delta \text{kappa} = K - K_0$, K_0 ,being the floor kappa number. K_0 depends on the type of fibers (HW, SW etc.) for a fully washed pulp ,pulping condition, control measures, lignin content and the type of lignin. Exact value of this parameter is generally not known.

4.4.4 Two parameter Model for AOX

Stromberg(110) reported that 1 kg of COD consumes about 0.4 to 0.8 kg of active chlorine. Similar report of 0.5-1 kg Chlorine requirements per kg of BLS is also found out by Nikki and Korhonen as mentioned by Kocurek(51).Lindstrom and Norden(62) also reported the value on the order of 0.5-0.6 kg active Cl₂.

Table-4.7 Chlorine consumption given by different investigators

Cl ₂ consumption, kg act. Cl ₂	Reference
0.4-0.8/ kg COD	Stromberg(110)
0.5-1.0/kg BLS	Kocurek(51)
0.5-0.6/kg COD	Lindstrom & Nordan(62)

Using this data, chlorine consumption in a chlorine based bleach plant can be fairly estimated. Eq.2 of Table-6 of APPENDIX-VIII for AOX model expressed as a function of chlorine consumption can be used without any significant error for practical calculations. This, in turn, can be described below as a function of washing parameters, namely ,DF and N. Thus the regression equations(Eqs.)developed using the principles laid down in APPENDIX-III can be used for estimating BOD for bleach plant. For this present calculation the average factor due Stromberg(110) 0.6 factor is used for AOX estimation. If one uses factor 0.5 due to Lindstrom and Norden(62), the value will obviously be lower.

$$AOX=0.271(DF*N)+0.417(N^2)-4.182(N)-3.774(DF)+0.358(DF^2)+17.903; R^2=0.988 \quad (4.34)$$

4.4.5 Two parameter Model Equations for BOD

BSW optimization requires the relationship of effluent parameters with washing parameters(DF,N).Using Eq.2 of Table-4.6 the various values of COD can be calculated as a function of DF and N.

Once the COD values are known, recourse can be taken care of the estimation of BOD from model of COD relating BOD.

With the variation of DF and N total solid loss with pulp from the last stage of BSW is obtained from algorithm-2 developed in Chap-2. By using Eq.2 of Table-4.6, one can calculate the COD various DF and N for an assumed kappa number 20 which are mostly used for HW and Bamb. Eq. 4.28 gives the best prediction of BOD from COD in terms of percent error and R^2 values. indicated, the equation gives close to 100% prediction within the normal range of COD and BOD values, even for CEDED sequence, it is quite reasonable to assume the value of COD nearly 3 times those of BOD atleast in bleach plant. The results obtained from Eq.4.28 is subjected multi-variate regression analysis and the model for BOD as a function of DF and N is developed as follows:

$$\text{BOD} = 2.635(\text{DF} \cdot \text{N}) + 3.222(\text{N}^2) - 32.987(\text{N}) - 30.819(\text{DF}) + 2.926(\text{DF})^2 + 125.135; r^2 = 0.975 \quad (4.3)$$

The model predicts both the values of BOD₅ and COD (DF= 2.5-4.5 and N=3 to4) within 14.9 kg/t and 58 to 41 kg/t respectively. This is verified from the works of many investigators(12,35,40).

Table- 4.8 BOD and COD consumption in bleach plant

BOD, kg/t		COD, kg/t		Reference
SW	HW	SW	HW	
11-32	6-12	57-105	25-50	Heimbürger(40)
16	-	80	-	Gullichsen(35)
9.30-11.93	-	28.25-34.82	-	Brunner(12)

Heimbürger et al.(40) reported the data of effluent loading from the experimental works of Liebergott(61) for both SW(kappa No=32) and HW(18.6-20) in the various conventional

bleaching sequences(without oxygen in pre-bleaching stage). It is found that the BOD values range between 6-12(HW) and 11-32(SW) whereas the respective values of COD lie between 25-50 and 57-105 kg/tonne. The BOD₇ and COD value are quoted by also Gullichsen(35)for standard Kraft without effluent treatment on the order of 24 and 100 respectively for a fully bleached SW pulp in which the bleach plant alone discharges 16 kg/t and 80 kg/t respectively. Brunner(12) reported the value of BOD 9.30-11.93kg/t and the same for COD equal to 28.25-34.82 kg/t. Therefore, these equations can be used safely for optimization purpose. As indicated above the model for AOX does not need any correction as it is the bleach plant which alone discharges AOX, the BOD is not. In fact, there are other sources of BOD typically for SW as shown in the block diagram(Fig.a). The total BOD load from other four sections for SW based pulp amounts to 28.3. The same for HW might be on the order 17-21 kg/t. This is corroborated from the data reported by UNEP(119). For CEDED sequence, the total mill effluent BOD₅ and COD for conventional bleach plant for hardwood has been reported as 29 and 81 kg/t₉₀ respectively. However, BOD₇ and COD for this sequence in bleach plant alone are found on the order of 10.1 and 42 kg/t respectively. In order to predict more accurately the total BOD₅ load entering to ETP, the equation.. is modified by adding the loads from other section(assuming 20 kg/t) can be rewritten as:

$$(BOD)_T = 2.593(DF \cdot N) + 4.053(N^2) - 40.415(N) - 36.116(DF) + 3.421(DF)^2 + 145.135; \quad r^2 = 0.988 \quad (4.36)$$

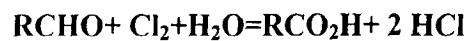
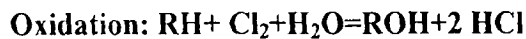
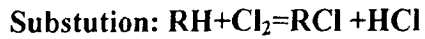
From the value of r^2 , it is very clear that both the correlations appear to be very good.

The above equation, thus can be used for optimization which will be dealt in Chap-6.

4.5 ESTIMATION OF CHEMICAL CONSUMPTION IN BLEACH PLANT

It is important to estimate the chemical consumption due to carry over solids and the accompanying cost for optimization of BSW operation. In order to accomplish this, one has to know the bleaching reaction taking place between lignin and chlorine. It is well known that two

basic chemical reactions occur in chlorination stage- the substitution and the oxidation. The former proceeds very rapidly at the start of the chlorination reaction while the latter follows throughout the entire reaction period. Shackford(97) assumed a 50/50 split in the two reaction mechanisms of the following types:



Where R is the benzene ring portion of the lignin molecule.

At the 50/50 substitution / oxidation ratio, 75% of the applied Cl_2 is assumed to be converted in the reaction to HCl and must be washed out or neutralized with caustic in the extraction stage.

In this present study an algorithm has been developed after slight modification of the concept put forward by Shackford(97). The previous model is based on kappa number only. In this present model additional term due to carry over solid has been introduced. From results of algorithm developed in Chap-2 and using the value of total solid loss for different dilution factor(DF) and number of washers(N) the following algorithm is developed to calculate the consumption of chemicals in bleach plant based on the principles given in Section 4.3.5

4.6 ALGORITHM TO CALCULATE THE NEUTRALIZATION COST DUE TO CARRY-OVER SOLIDS IN BLEACH PLANT

In the development of the algorithm, the total solid going with the pulp is symbolized as X kg/t while the % lignin , % carbohydrates, washing efficiency are y, z and η respectively. The logical steps are as under:

Step-1 Calculation of lignin content and carbohydrates in black liquor, kg/tonne

lignin content $L_c= X * y$

carbohydrates $C_c= X * z$

Step-2 Chlorine consumption in substitution reaction, kg/tonne pulp

$$C_{LS} = (M_{Cl} / M_{lig}) * L_c$$

Step-3 Applied chlorine to generate the hydrochloric acid, kg/tonne pulp

$$AC_{LS} = (C_{LS} / F_r)$$

Step-4 Hydrochloric acid generated in substitution, kg/tonne pulp

$$HCl_{LS} = (M_{HCl} / M_{Cl}) * AC_{LS}$$

Step-5 Hydrochloric acid generated in oxidation of lignin, kg/tonne pulp

$$HCl_{LO} = 2 * HCl_{LS}$$

Step-6 Chlorine consumption in oxidation of carbohydrates, kg/tonne pulp

$$C_{CO} = (M_{Cl} / M_C) * C_C$$

Step-7 Applied chlorine to generate the hydrochloric acid, kg/tonne pulp

$$AC_{CO} = C_{CO} / F_r$$

Step-8 Hydrochloric acid generated in oxidation, kg/tonne pulp

$$HCl_{CO} = 2 * (M_{HCl} / M_{Cl}) * AC_{CO} \text{ kg/ton}$$

Step-9 Total Hydrochloric acid generated, kg/tonne pulp

$$HCl_T = HCl_{LS} + HCl_{LO} + HCl_{CO}$$

Step-10 Carry over with the pulp, %

$$C_o = 100 - \eta$$

Step-11 HCl carry over with the pulp, kg/tonne pulp

$$HCl = HCl_T * C_o / 100$$

Step-12 Caustic required to neutralize the HCl carry over, kg/tonne pulp

$$NaOH = (M_{NaOH} / M_{HCl}) * HCl$$

Step-13 Total chemical consumption due to carry over, kg/tonne pulp

$$TCC = AC_{LS} + AC_{CO} + NaOH$$

Based on the model using C++ computer program, results has been obtained. These are interpreted through various plots as shown below:

(a) Effect of DF on NaOH consumption in bleach plant:

For each particular dilution factor, there is a corresponding solid loss (Fig.2.1). To neutralize the carry over solids(COD), sodium hydroxide consumption is calculated from model given Section.. From Fig.4.15, it is observed that the increase in dilution factor results in decrease sodium hydroxide consumption in bleaching. The trend of the curve is asymptotic in nature. On close scrutiny of the results, it is found that there is insignificant sodium hydroxide consumption for dilution factor 4.0

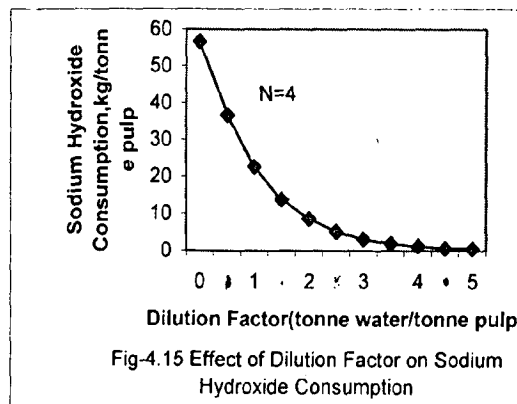


Fig-4.15 Effect of Dilution Factor on Sodium Hydroxide Consumption

(b) Effect of Discharge Consistency on NaOH Consumption:

Fig.4.16 shows the effect of discharge consistency on sodium hydroxide consumption

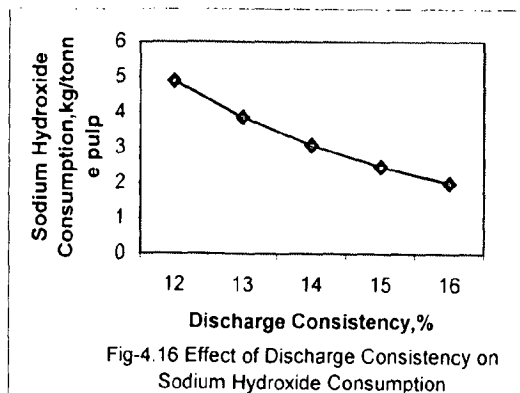
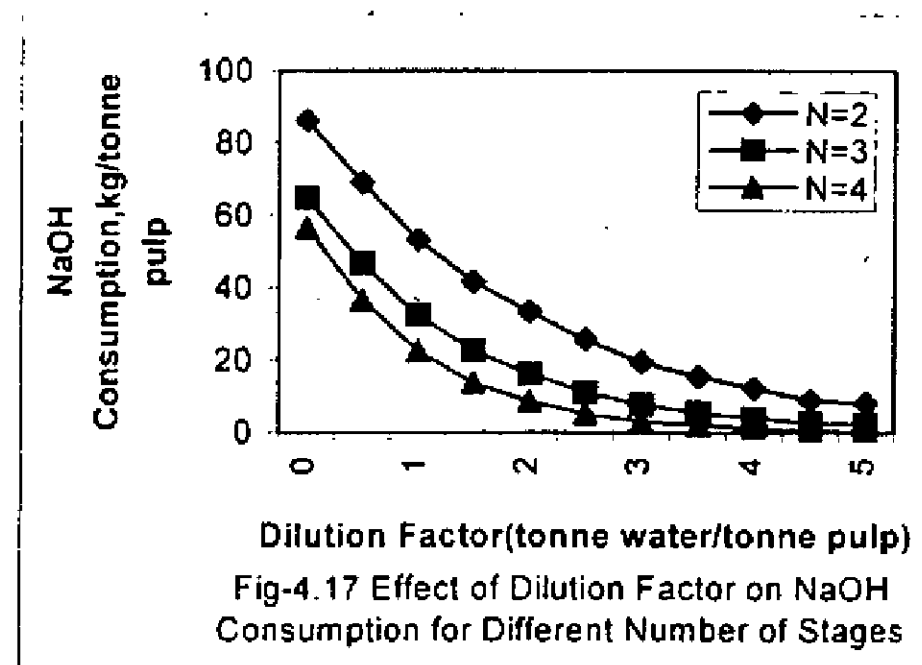


Fig-4.16 Effect of Discharge Consistency on Sodium Hydroxide Consumption

With the increase of discharge consistency, there is a decreasing trend of total solid loss. From figure, it is evident that the increase in discharge consistency results in decreased sodium hydroxide consumption. The trend of the curve is similar to those of Fig.2.9.

(c) Combined effect of DF and Number of stages(N) on NaOH Consumption in bleach Plant:

Fig.4.17 describes the effect of dilution factor on NaOH consumption kg/t pulp.



It is evident from the figure that with the increase in dilution factor, NaOH consumption, kg/tonne pulp will be decreased. This NaOH is used to neutralize the total solid out with the sheet kg/tonne pulp. If dilution factor increases, the maximum amount of dissolved organic and soluble inorganic material present with the pulp will be removed. Therefore, a minimum amount of solids will go out with the pulp. For minimum solids, minimum amount of NaOH is required. Similarly, with the increase of number of washers, NaOH consumption will be decreased for a fixed dilution factor. With the increase of number of washers, the solid with the pulp decreases and hence NaOH consumption decreases.

4.7 CONCLUSION

- A modified form of non-linear system model of a multi-stage bleach plant has been developed based on the guide lines of previous workers for optimization. For mere convenience CEDED has been taken as an example. The optimization scheme of Freedman

CHAPTER-5

MATHEMATICAL MODELING FOR COMBUSTION OF BLS

5.0 INTRODUCTION

The combustion of concentrated pulping spent liquors is one of the central unit operations in all chemical recovery processes. This operation will often prove to be an economically feasible method of reducing the stream pollution of the pulp mill, because it makes it possible to regenerate the pulping chemicals and simultaneously to utilize the fuel value of the spent liquor. The principles of recovery operations and the important parameters in detail have been dealt in Chap-1. In this present investigation, the estimation of heat value of washable black liquor solids including lignin along with the black liquor from BSW as a function of DF and N is only to be attempted. The lignin and carbohydrates present in BLS will release heat when it burns in recovery boiler-furnace. The heat value of BLS vis-a-vis lignin in terms of steam production as a function of Dilution factor and number of stages in BSW operation will be used in the subsequent optimization program. Therefore, the modeling of heating value of BLS needs to be exercised in this chapter. There are many models reported in the literature so far. These require a close scrutiny for their suitability in application. An attempt is thus made in this study to examine the relevant aspects of strong and heavy black liquor before undertaking the models. In the following paragraphs these are reviewed.

5.1 PROPERTIES OF STRONG BLACK LIQUOR

The thermal and transport properties of black liquor directly affect evaporator and recovery boiler design, operation and optimization. As indicated, in this present section with regard to combustion, only the modeling of heating value of concentrated black liquor is considered. The other properties like physical, transport and chemical properties are already discussed in Chap-3,

Section-3.1 while describing the various models for weak black liquor entering to the MEE. These are equally applicable to strong black liquor also.

5.2 MODELING OF HEATING VALUE OF BLACK LIQUOR SOLIDS

It is a fact that heating value of the liquor has a large impact on the steam generation rate and on the maximum pulp production rate that a boiler can support. In evaluating the impact of process changes, it is important to accurately estimate the heating value of black liquor /black liquor solids from knowledge of the pulping conditions, raw materials, pulp yield and elemental composition of BLS. There is no correlation available relating the above variables. However, the compositions of raw materials are known though these vary even with the same species. It is interesting to note that while most of the hardwood species including Eucalyptus the lignin content lies between 20-24% whereas Eucalyptus hybrid is reported to contain the same on the order of 30.90% as reported by Veeramani(121). These varying values has defied the development of higher order intricate multivariable statistical correlation. It is well known that black liquor is a complex material. It's complete composition is not known yet. Therefore, it is not possible to treat this subject very rigorously. Very few investigations have been made with determination of all(or the major proportion) of the black liquor constituents. It seems that this is mainly attributable to the black liquor being a colloidal solution of a nature which alters rapidly by many reactions (oxidation, condensation etc.) after the cook. The data are however, mainly available for softwoods reported by Passinen(74) based on the experimental works due to Enkvist, Komshilov and Letonmaki. On the other-hand, there is no such detailed analysis is available for hardwood and bamboo species. However, the percentage of the components of black liquor between hardwood and softwood does not seem to vary greatly if one calculates on dry solid basis. In the present investigation the data reported by Passinen(74) is used. This is given in Table-1 in APPENDIX-IX.

The heating value of black liquor solids derives almost entirely from its organic content. individual component has its own particular heating value. The heating value of some components of black liquor given in the Table-5.1 is reported by Fredrick(22). This can be the basis for calculation of heating value in the present study without erring widely.

Table-5.1 Black liquor component heating value

Component	Heating value, kJ/kg
Softwood lignin	26283.8
Hardwood lignin	24655.6
Carbohydrates	17212.4
Extractives	39309.4
Na ₂ S	13025.6
Na ₂ S ₂ O ₃	5791.74

The heating value depends on the elemental composition of black liquor solids. The same can be easily estimated once summative elemental composition is known. Fortunately large body of literature are reported for softwood BLS, the same for hardwood and bamboo is scarce. Table-5.1 indicates a typical set of data averaged for hardwood and bamboo from Indian mill. In this present study these are used for calculation.

There are two kinds of heating value HHV and NHV. Typical values for the HHV of Kraft black liquor generally lie between 13,400 and 15,500 kJ/kg of black liquor solids. Both are used by different investigators for calculation of steam generation in recovery-boiler-furnace system.

Table-5.2 Elemental composition of BL

Element	Percentage
Carbon(C)	33.22
Hydrogen(H)	3.665
Nitrogen(N)	0.235
Sodium(Na)	19.115
Sulphur(S)	3.57
Potassium(K)	3.645
Chloride(Cl)	0.435
Oxygen(O)	35.49
Other inorganics	0.135

The procedure of estimation of the heating value is found elsewhere(32). The relation between NHV and HHV are given as under:

$$\text{NHV}=\text{HHV}-2440[(18/2)(\%H/100)+(100-\%s)/\%s]-12900[(78/32)(\%s/100) (\%reduction/100)]$$

NHV is usually found to be approximately 20% less than the HHV. It is obvious that the steam generation value will be higher if one calculates based on HHV. Measurement of HHV are generally made in an oxygen bomb calorimeter using oxygen substantially in excess of the stoichiometric requirement. Differences in the final state of the combustion products between the oxygen bomb calorimeter measurement and the actual boiler operation cause the actual heat release to be less than the measured HHV.

It is evident from Table -5.1 that softwood lignin has a higher heating value than hard wood lignin and agri-residue based non-wood lignin because of the higher methoxyl content of the former

compared to that of the hard wood lignin and bamboo. Non-wood lignin is, however, mainly composed of para hydroxy phenyl propane units and give much lower than those from the softwood and hardwood species.

However, the actual heating value will depend on hardwood/softwood ratio, the relative proportion of lignin and carbohydrate(species and yield), degree of oxidation of the liquor exposed to oxidizing atmosphere, the amount of dead load inorganic chemicals, and the degree of soap removal(if any).

Recovery boiler designs are often based on a heating value of 15351.6 kJ/kg liquor solids. Very few liquors have a heating value of this high magnitude. More typically softwood black liquors have HHVs in the range of 14653.8 to 14886.4 kJ/kg whereas the same for hardwood and bamboo liquors is found in the range of 13490-13956kJ/kg. Heating value of liquors actually fired into furnace are even lower because of dilution with recycled ash from the precipitator, economizer and saltcake addition in the mixing tank.

Over the years the models(mathematical/empirical)are remodified and used in the estimation design calculation. The following methods are available for modeling heating value of black liquor solids

- a. Models based on total enthalpy due to Gullichsen(34)
- b. Models related to the composition and fuel value of black liquor due to Annergren et al.(3)
- c. Models of calorific value of spent liquor through carbon analysis due to Mc Donald(67)
- d. Models proposed by Green and Grace (32)
- e. Modified Green and Grace method proposed by Frederick(22)

The merits and demerits of all the above methods are discussed briefly in the following paragraphs:

5.2.1 Estimation of Heat Values and Recoverable Heat By the Total Enthalpy Method

This method of total enthalpy has proved useful in many fields of the chemical industry. Gessner(74) has initially developed this method using heat of formation as the enthalpy change produced when one mole of any compound is formed from its elements at 25⁰C and at atmospheric pressure. This method is thus useful only when the total enthalpies for all components involved are known or possible to derive. If the chemical composition of black liquor is known, it is possible to assess its heating value or to estimate the recoverable heat in the combustion process in recovery furnace. The total enthalpy, H, kJ/kg represents the sum of the isothermal heat of formation(i.e. enthalpy change caused by formation of any compound from its elements at 25⁰C and at 1 atm. pressure), sensible heat above the reference temperature, latent heat of fusion or evaporation and heats of solution and dilution. Mathematically, it can be expressed as

$$H = \Delta H_{f, 298K, 1atm} + \int_{298K}^{T^2} C_p dt + \Delta H_{agr} + \Delta H_S$$

The pressure effect on the total enthalpies has proved negligible for substances present in spent liquors. The element states for compound present in spent liquors are gaseous H₂, O₂, N₂, solid C (graphite), Na (or Ca, Mg) and S(rhomic).

The transformation of energy Q for any chemical reaction is the differences between the sum of the total enthalpies of the reactants and the corresponding sum of the reaction products. In mathematical form,

$$Q = \Sigma H_{in} - \Sigma H_{out}$$

The heat of formation and total enthalpies of all the organic compounds in the black liquor are unfortunately not reported in the literature and requires precise derivation.

5.2.2 Models Proposed by Mc-Donald(67)

Heating values of black liquor at different percent solids have been plotted as functions of

percentage of total carbon(TC), percentage of total organic carbon(TOC), and percentage organics(Organics) by Mc Donald(67). These are reproduced below.

(a) $\text{Btu/lb of liquor} = 166 * (\text{TC}) + 39$

(b) $\text{Btu/lb of liquor} = 92.5 * (\text{Organics}) + 6$

(c) $\text{Btu/lb of liquor} = 170 * (\text{TOC}) + 44$

Similar equation has also been reported by Ray et al.(87) as follows

(d) $\text{BHV, kCal/kg black liquor solids} = 53.31 + 94.59 * C$

The Eqs. (a) to (d) suffers from the limitation that they are function of one constituent only and related to the other pertinent composition or pulping conditions. Hence can not be used modeling.

5.2.3 Modified Models for Heating Value of Black Liquor Solids

The most up- to- date models are those proposed by Green and Grace and their modified forms. In actual operation for calculation of heating value of black liquor solids, the analysis of black liquor data must be needed. This, in turn, depends upon the raw material used, pulping conditions, the pulp yield, kappa no., lignin content in raw material as well as in pulp, volatiles organics including resins, fatty acids, carbohydrates and tall oil contents(if any). The influence of active alkali, sulfidity, sodium sulphide, sodium carbonate, sodium sulphate, are also to be introduced in the model. Additional terms like causticity, sulphur reduction and unbleached washing efficiency, are also to be considered. As a matter of fact, the models due to Green and Grace and their modifications have included the above parameters.

5.2.3.1 Green and Grace Model

Green and Grace(32) developed a worksheet to calculate heating value of black liquor from knowledge of the pulping conditions. Their procedure is based on the following assumptions.

1. The heating value of black liquor solids is equal to the sum of the products of the heating value of individual component times their mass fractions.
2. The sulfur compounds for unoxidized liquors have 85% of the heating value of sodium sulfur.
3. The black liquor composition is determined by mass balance around the digester. Three items are subtracted from the solids input of wood and white liquor, water formed by neutralization of NaOH by wood acids, volatiles lost when the digester is blown, and tall oil soap(if any) is removed. The water formed by neutralization is assumed to be of the order of 150lb/ton for white liquor or 130 lb/ton for orange liquor. The other losses are based on typical values for the specific mill application.
4. Oxidation reduces the heating value of black liquor by an amount 30% greater than the heat that would be released by the conversion of sodium sulfide to sodium thiosulfate. This is due to partial oxidation of the organics.

Fredrick(22) have reported the limitation of Green and Grace procedure. Green and Grace's procedure does not account for the effect of differences in sodium carbonate or sodium concentrations in white liquor. The modifications allow a correction for white liquor causticity and sulfur reduction efficiency.

5.2.3.2 Black Liquor Heating Value (HHV) Calculation

From literature survey, it is evident that the modification of Green and Grace(32) method for dead load put forward by Frederick(22) is most sophisticated. Therefore, in this present investigation, this model is used as a basis for further improvement To estimate the heating value of BLS an algorithm is developed for HHV(algorithm-1) based on Green and Grace procedure as this is now the most commonly used method for estimation of heating value for steam generation calculation. This algorithm can be used in this present study to examine the effect of sulphidity, active alkali and yield on heating value of BLS. As algorithm 1 needs raw material quality and pulping process

condition it can not be used as such without detailed material balance across the digester specific raw material and their yield values.

As this present problem deals with washing and its subsequent stages another model is required to develop which can inter-link the washing parameter with combustion of BLS. The model 2 thus be used for detailed calculation. This is essential as Green and Grace method and its modified form do not relate to washing parameters like DF, and N. These require to be incorporated into the model. Based on the above concepts, algorithm-2 is developed as shown below. The algorithm is in fact, the excerpts from the algorithm -1 to evaluate the heating value from the knowledge of black liquor composition and heating value of components of black liquor solids.

Both the algorithms(algorithm -1 and 2) can be subjected to computer program for acquisition of data using C++ language.

5.3 MODELING FOR ESTIMATING HEAT VALUE OF BLS AS A FUNCTION OF DILUTION FACTOR

5.3.1 Development of Algorithm Based on Frederick Model(22)

5.3.1.1 Algorithm-1

The step by step procedure are as follows:

STEP-1. Bleached pulp, od tonne/day,

$$P_{od} = P_{ad} \times 0.90$$

STEP-2 Unbleached pulp, od tonne/day,

$$UP = (100 \times P_{od})/Y_B$$

STEP-3. Wood used, od tonne/day,

$$W_0 = (100 \times UP)/Y_{UP}$$

STEP-4. Wood used, od kg/od tonne UP,

$$W_{UP} = (W_0 \times 2000)/UP$$

STEP-5. Volatiles lost , od kg/od tonne UP,

$$V_{UP} = W_{UP}/100$$

STEP-6. Organics in BL, od kg/od tonne UP,

$$O_{BL} = W_{UP} - 2000 - V_{UP}$$

STEP-7. Lignin in wood, od kg/od tonne UP,

$$L_{od} = (L_w \times L_{UP})/100$$

STEP-8. Lignin in BL, od kg/od tonne UP,

$$L_{UP} = 3 \times K_a$$

STEP-9. Miscellaneous, organics in BL, od kg/tonne UP,

$$L_{BL} = L_{od} - L_{Up}$$

STEP-10. Miscellaneous organics in BL, od kg/od tonne UP,

$$O_m = y \times W_{UP}$$

STEP-11. Resins, fatty acids, od kg/tonne UP,

$$O_{r,f} = Z \times W_{UP}$$

STEP-12. Tall oil recovered, od kg/od tonne UP,

$$O_{to} = v \times W_{UP}$$

STEP-13. Resins fatty acids in BL od kg/od tonne UP,

$$Rf_{BL} = O_{rf} - O_{to}$$

STEP-14. Organics acid from carbohydrates in BL, od kg/od tonne UP,

$$O_C = O_{BL} - (L_{BL} + O_m + O_{r,f})$$

STEP-15. Total organics in BL, od kg/od tonne UP,

$$T_o = L_{BL} + O_m + Rf_{BL} + O_C$$

STEP-16. Heating value of lignin,

$$THV_{lig} = L_{BL} \times HV_{lig} \text{ kJ/od tonne UP}$$

STEP-17. Heating value of miscellaneous organics,

$$THV_{m0} = O_m \times HV_{m0} \text{ kJ/od tonne UP}$$

STEP-18. Heating value of resins, fatty acids,

$$THV_{r,f} = Rf_{Bl} \times HV_{r,f} \text{ kJ/od tonne UP}$$

STEP-19. Heating value of organic acids from carbohydrates,

$$THV_{oa} = O_C \times HV_{oa} \text{ kJ/od tonne UP}$$

STEP-20. Total heating value of organics in BL,

$$HV_o = THV_{lig} + THV_{mo} + THV_{r,f} + THV_{oa} \text{ kJ/od tonne UP}$$

STEP-21. AA applied, as Na₂O, od kg/od tonne UP,

$$N_{AA} = (AA \times W_{UP})/100$$

STEP-22. Na₂S applied, as Na₂O, od kg/od tonne UP

$$N_S = (N_{AA} \times SL)/100$$

STEP-23. Na₂CO₃ in WL, od kg/od tonne UP

$$N_{CO_3} = 1.71 \times (N_{AA} - N_S) \times (100 - C_{Na})$$

STEP-24. Na₂SO₄ in WL, od kg/od tonne UP

$$N_{SO_4} = 2.29 \times N_S \times (100 - S_r)/S_r$$

STEP-25. Total inorganic solids, od kg/od tonne UP

$$T_{ino} = 1.29 \times N_{AA}(1 - SL/100) + 1.26 \times N_S + N_{CO_3} + N_{SO_4}$$

STEP-26. Total BLS, od kg/od tonne UP

$$T_{BL} = T_o + T_{ino} - W$$

STEP-27. Organics in BL, %

$$O_{BLS} = (T_o \times 100)/T_{BL}$$

STEP-28. Inorganic heating value kJ/od tonne UP

$$THV_{ino} = N_S \times HV_{ino}$$

STEP-29. Total heating value, kJ/od tonne UP

$$HV_T = HV_0 + THV_I$$

STEP-30. Solids heating value, kJ/kg BLS

$$HV_S = HV_T / T_{BL}$$

STEP-31 Obtain a functional relationship(nonlinear regression equation)among the W_e , DF and N.

STEP-32 Total BLS to boiler, od kg/od tonne UP

$$T_{BOS} = (T_{BL} \times W_e(DF,N)) / 100$$

STEP-33 Total BL to boiler, od kg/od tonne UP

$$T_{BOL} = (T_{BL} \times W_e) / T_{BLH}$$

STEP-34 BL firing rate, kg/min.

$$FR = (T_{BOL} \times UP \times 7.48) / 1440 \times P_{BL}$$

STEP-35 Boiler load , kJ/od tonne UP

$$BL_0 = (HV_T \times W_e) / 100$$

STEP-36 Boiler load, kJ/min.

$$BL_1 = (BL_0 \times UP) / 1440$$

Note: In step 8 the amount of lignin in percentage has been assumed around two times of the theoretical equations (lignin % in pulp=0.147*kappa number) which is not far from the practice.

5.3.1.2 Development of Algorithm-2

Step-1 Calculate BLS for various dilution factor(DF) and number of stages using material balance in Chap -2(Section-2.2.2)

Step-2 Calculation of lignin in Black Liquor, od kg/od tonne pulp

$$L = BLS * X * 1000$$

Step-3 Calculation of miscellaneous organics in Black Liquor, od kg/od tonne pulp

$$MO = BLS * y * 1000$$

Step-4 Calculation of Resins, fatty acids in Black Liquor, od kg/od tonne pulp

$$RF = BLS * Z * 1000$$

Step-5 Calculation of Organic acids from carbohydrates in Black Liquor, od kg/od tonne pulp

$$OA = (BLS * w)$$

Step-6 Calculation of total organics in Black Liquor, od kg/od tonne pulp

$$To = L + MO + Rf + OA$$

Step-7 Calculation of Heating value of lignin, kJ/od tonne pulp

$$THV_{lig} = L * HV_{lig}$$

Step-8 Calculation of heating value of miscellaneous organics, kJ/od tonne pulp

$$THV_{MO} = MO * HV_{MO}$$

Step-9 Calculation of heating value of resins, fatty acids, kJ/od tonne pulp

$$THV_{r,f} = Rf * HV_{r,f}$$

Step-10 Calculation of heating value of organic acids from carbohydrates, kJ/od tonne pulp

$$THV_{OA} = OA * HV_{OA}$$

Step-11 Calculation of total heating value of organics in Black Liquor, kJ/od tonne pulp

$$HV = THV_{lig} + THV_{MO} + THV_{r,f} + THV_{OA}$$

Step-12 Calculation of Na₂S in Black Liquor, od kg/od tonne pulp

$$NS = V * BLS$$

Step-13 Calculation of heating value of Na₂S, kJ/od tonne pulp

$$THV_S = HV_S * Na_2S$$

Step-14 Calculation of Na₂S₂O₃ in Black Liquor, od kg/od tonne pulp

$$NSO=U*BLS$$

Step-15 Calculation of heating value of $Na_2S_2O_3$,kJ/od tonne pulp

$$THV_{SO} = HV_{SO} * NSO$$

Step-16 Calculation of total heating value of inorganics in Black Liquor, kJ/od tonne pulp

$$HV_i = THV_s + THV_{SO}$$

Step-17 Calculation of total heating value, kJ/od tonne pulp

$$HV_T = HV + Hvi$$

Step-18 Develop Multiple linear regression in heating value of black liquor

solids ,DF and number of stages using data in Table-2 in APPENDIX-IX.

Step-19 Assume Enthalpy per kg of steam delivered to mill = Δh

Step-20 Steam delivered to mill = heat to steam/enthalpy per kg of

$$Q_{bls} / \Delta h \text{ kg/ kg BLS}$$

It is evident from the model that in Step-31 in algorithm-1 and Step-1 in algorithm-2 some statistical regression equations are introduced. This modification of the model therefore, generalizes the relationship between BLS, DF and N. Hence, the heating value is expressed in terms of washing process and its design parameters in the present model.

5.4 RESULTS AND DISCUSSION

5.4.1 Validity of Algorithms

The algorithm requires validation. For this purpose, the parameters including unbleached pulp yield reported by Frederick is used in the C++ program. The algorithm-1 predicts accurately the values of total heating value, total BLS, boiler load per tonne of unbleached pulp and solids heating value per kg of BLS. It is thus amply clear that the algorithm developed and the computer program made is correct. The algorithm -2 does not require any validation.

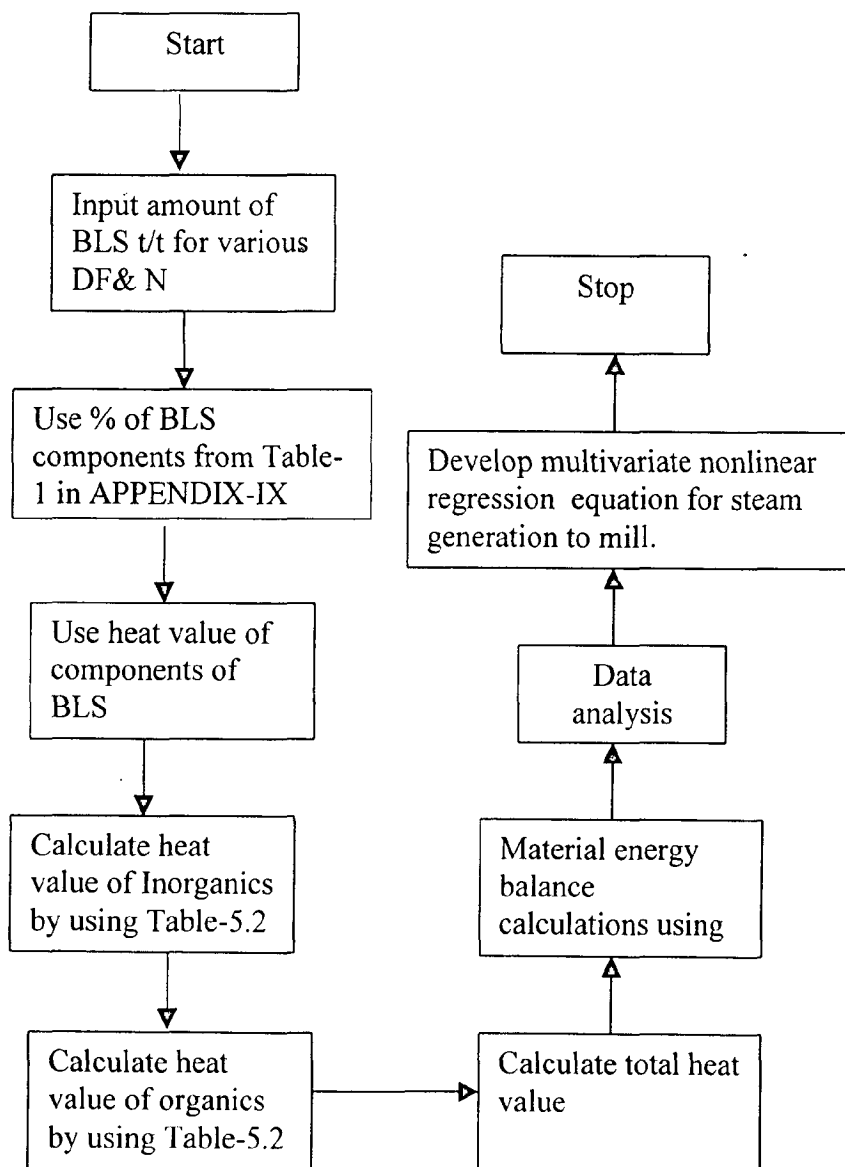
Steady state material balance for number of washers, N and various dilution factors, DF give liquor and solid entering to MEE. Using the value of black liquor solids/t , heating value of liquor is obtained This in turn employed to estimate steam generation. For the above purpose of Passinen(74) for all the organic constituents of BLS, data of Na₂S, and Na₂ S₂O₃ Macdonald (64), data of Frederick(22) for component heating value from Table-5.1. and the elemental composition of BLS obtained from Indian Industry(Table-5.2) are used. The operating parameters for material and energy balance for the simulation in the present work is shown in following Table.

Table-5.3 Operating parameters for recovery furnace

Parameters	Values
Excess FD air, %	8
Infiltration air, %	12
Total excess air, %	20
Ambient temperature, °C	27
Humidity of air, kg/kg dry air	0.018
FD air preheat temperature, °C	150
Firing black liquor conc. %	65

These data are normally prevalent in most of the Indian bamboo and hardwood based mills therefore are quite reasonable for present assumption. Material balance for smelt, stoichiometric combustion products, air requirements, water vapor in stack gas from water ,moisture addition flue gas generated is made. This is then followed by energy balance using heating value of sensible heat in black liquor, air, and to preheat air, heat in blow down,, soot blowing steam , combustion heating steam, and heat in air humidity, sensible heat in dry flue gas, and smelt, heat loss

hydrogen in BLS, and water in BL, heat loss from sulphite, and radiation loss etc. In this present study all possible accountable losses are considered based on Kocurek(51),Gerald(43), Macdonald(64) and Frederick(22). It is important to note that some have neglected few terms while other have accepted the same while attempting detailed energy balance calculations. It is also interesting to know that generally the heating value of BLS is on the order of 93.5%-94.3% of total heat input to the furnace and the steam flow to mill ranges between 3.23 to 3.86 for a well balanced system. A flow diagram indicating the sequence of calculation is shown below:



Based on the algorithm-2 a computer program using C++ language is also developed to calculate heating value of black liquor solids, material and energy balance for the recovery boiler-furnace and steam production therefrom. The data from the present investigation evolved out from material and energy balance calculation and further employed in algorithm is shown in Table-5.4.

Table-5.4 Heat input in recovery furnace

Heat input	kJ/kg BLS
Sensible heat in BL	244.850
Sensible heat in air	9.057
Heat to preheat air	510.629
Heat in feed water soot blowing steam	74.325
Heat in blow down	39.176

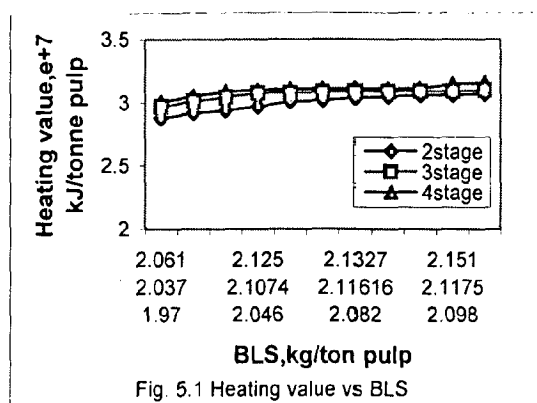
Table-5.5 Heat loss in recovery furnace

Heat loss	KJ/kg BLS
Sensible heat in dry flue gas	888.709
Heat loss from hydrogen in BLS	920.207
Heat loss from water in BL	1502.415
Sensible heat in smelt	637.745
Heat to form sulphite	119.97
Heat loss from soot blowing steam	574.78
Heat loss from direct heating steam	159.04
Heat loss from air humidity	200.89
Radiation loss	3.5234
Unaccounted losses	23.4895
Blow down loss	126.5

These are compared with those of other designers. A representative sample of computed results as a function of DF and N is also given in APPENDIX-IX. The data are then interpreted in terms of plots for examining the parametric effects. These are detailed below:

5.4.1 Effect of BLS on Heating Value as a Function of Number of Stages

Fig. 5.1 describes the effect on total heating value of per tonne of pulp with number of stages as parameter. It is evident from the figure that with the increase of BLS there is slight enhancement



of HV. Similarly, if one intends to increase the number of stages increase of HV is noticed slightly.

5.4.2 Impact of Percent Sulphidity on Heating Value of BLS

From algorithm -1 the data of HV as a function of percentage sulphidity is generated. The parametric effect is shown in Fig.5.2. The figure demonstrates that the sulphidity enhances the heating value with strong linear characteristics. On closer scrutiny of the results and the curve it is clearly visible that with the 20%(20-40%) increase in sulfidity, increase of heating value kg/t pulp is of the order of 4.17%.

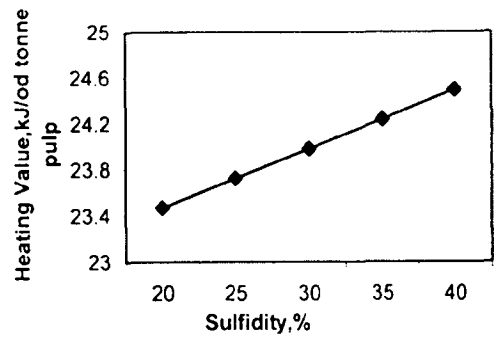


Fig. 5.2 Impact of sulfidity on black liquor heating value

5.4.3 Effect of Active Alkali Charge on Heating Value of BLS

Algorithm -1 is also used to examine the influence of active alkali on HV of BLS The relation is shown in Fig.5.3

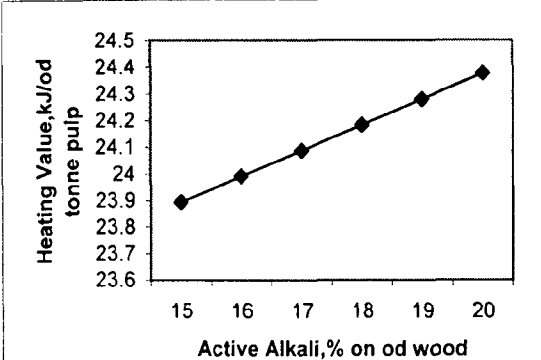


Fig. 5.3 Impact of active alkali charge on black liquor heating value

It is clear from the figure(Fig.5.3) that the heating value of BLS rises with the increase of a alkali charge. With the rise of AA of 5% the heating value of BLS increases by nearly 1.97% is contrary to some findings ,reported by Adams(1). However, the results from pr investigations agree with some of the experimental data of Passinen(74) as shown in the follo Table.

Table -5.5 Experimental data of Passinen(74) for heating value as a function of AA

Wood Species	Active Alkali, % asNa ₂ O	Calorimetric Heat ,kJ/kgBL
Spruce	11.0	15410.8
	12.1	16751.6
	13.0	16877.3
Scots Pine	12.4	15544.9
	13.2	15796.3
Poplar	6.0	14141.3
	9.0	14371.7
	12.0	15431.8

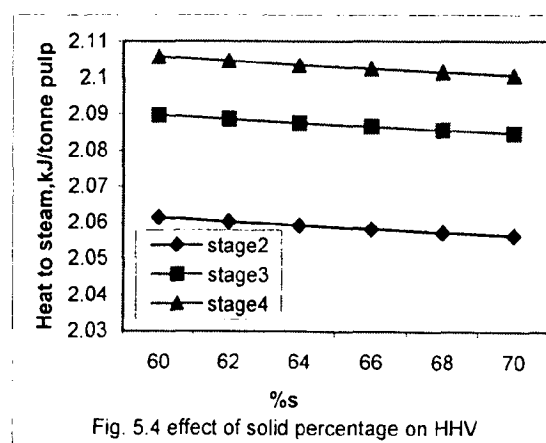
As a matter of fact ,in practice both might be true based on some situations. This can be explained by the fact that more alkali addition at a fixed temperature and pressure in digester will not only reduce the pulp yield and the accompanying lignin but also degrades the hemi-cellulose especially and to some extent also the α cellulose content of raw material, resulting in increase in organic content in black liquor, thereby enhances the heating value of BLS. It is already indicated that it is the organics which is responsible for increase of heating value. On the other hand, more alkali addition indicates the rise of inorganic content in the black liquor solids which obviously reduces the heating value. In that argument , the result of Adams(1) may also be valid. In fact, it is the relative contribution of two oppositely behaving components of BLS i.e. increase of organics or

increase in inorganics which tends to increasing or decreasing trends of the linearity. This requires estimation on case to case basis taking into account all the possible variables like the variation in raw material, its pulping conditions, relative amount of extra active alkali addition and complicated reaction kinetics of delignification and finally the selectivity.

5.4.4 Effect of Black Liquor Concentration on Heat Utilized for Steam Generation Recovery Furnace

The influence of heavy black liquor concentration in terms % solids on HHV is shown in Fig. The figure reveals the followings.

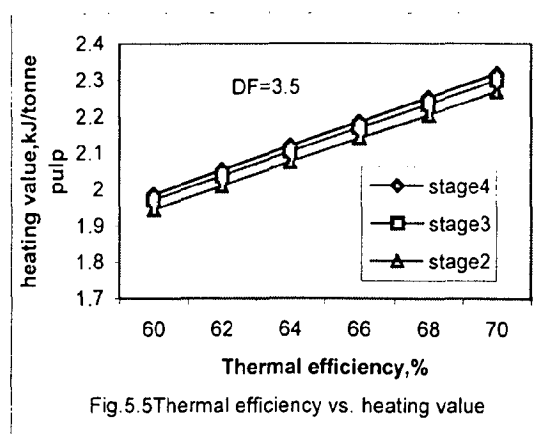
Increase in percentage solids of black liquor will decrease the HHV slightly. If one increases the number of stages of BSW, the heat utilized for steam generation, will, however increase. For three and four stage washers, increase in percentage solids of black liquor (within the range between 60% to 70%) decrease of HHV is approximately 0.1146, 0.1552, 0.2435% respectively. Increase the number of stages of BSW from 2 to 3 and 3 to 4, increase of HHV are of the order 1.34%, 0.75% respectively.



For more understanding of this parametric effect, detailed analysis on air, black liquor efficiency on heat utilization are required.

5.4.5 Effect of Thermal Efficiency on Heating Value of BLS

From algorithm -2 ,the data indicating the effect of thermal efficiency of recovery-boiler furnace on HV of BLS used to produce steam are generated. The range assumed in the algorithm is



between 60%- 70%. This is not far from the reality as the efficiency values in mills with recovery furnace normally lie 58%-68.5%, the average being 63.5% The relationship is shown in Fig.5.5. The plots reflect that with the increase of thermal efficiency the heating value utilized to steam increase in a linear manner. The influence of number of stages in BSW is also shown therein. As expected, the value becomes higher, if one goes on adding the number of stages in BSW system. It has been noticed that with the variation of thermal efficiency(60-70%) the heating value decreases to the extent of 14.28% for two, three and four stage washers. Nearly 1.35% and 0.75% heating value is increased if one intends to increase the N from 2 to 3 and 3 to 4 respectively.

5.4.6 Effect of Dilution Factor and Number of Stages on , Yield of Lignin, BLS, and Its Heating Value

The plots 5.6 through 5.8 are drawn to show the effects of DF on lignin yield, BLS, and HV respectively with number of stage as parameter.

Fig.5.6 is a plot between DF and lignin yield with varying number of stages of BSW.

It is reflected from the figure that higher the dilution factor higher amount of lignin is available BLS. An initial rapid change is noticed from DF from 0.0 to 2. Beyond DF=2, the value becomes almost constant. This is valid for all the designs of BSW system. As expected, higher the stage more will be the lignin extracted, increasing its yield. It is evident from the figure that for three and four stage washers lignin yield increases of the order of 6.32, 3.97, 4.725% respectively. It is interesting to note that if one increases the number of stage of washers from 2 to 3 and 3 to 4 the yield of lignin will be increased 2.07% and 0.797% respectively for DF=2.5.

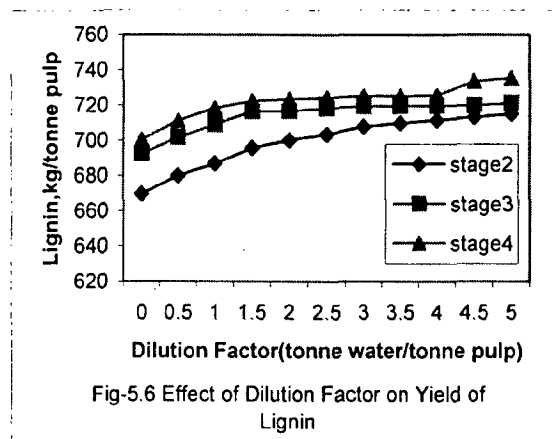
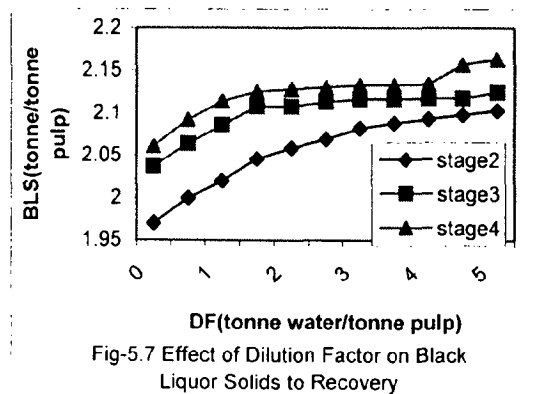
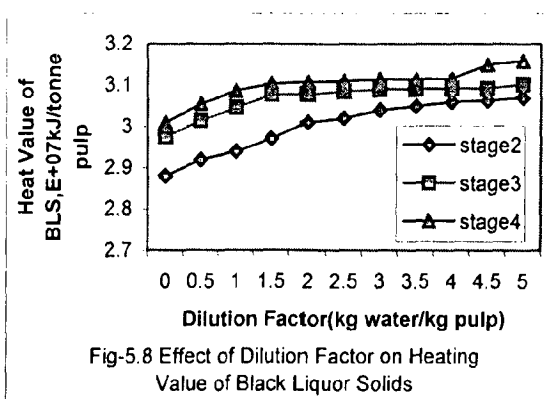


Fig.5.7 shows the effect of dilution factor on BLS to recovery. It is evident from the figure that we go on increasing dilution factor, total black liquor solid t/t pulp will be increased. With the



increase of number of stages at a fixed dilution factor BLS increases. There is no significant increase of BLS between dilution factor 2 to 4. But a rapid change in BLS to recovery is observed between DF 4 to 5. It has been noticed that BLS for two, three and four stage washers, increases to the extent of 6.32%, 4.1% and 4.72% respectively with the variation of dilution factor from 0 to 5. For a particular DF=2.5 with the increase of number of washers from 2 to 3 and from 3 to 4, an increase of the order 2.08% and 0.798% respectively is noticed.

It is evident from the figure(Fig.5.8) that with the increase in dilution factor there will be an increase in heat value of BLS/tonne of pulp for all the stages, higher for the greater number of stages. This is an expected trend as the dilution factor goes on increasing, total solid content tonne/tonne of pulp will be increased and hence heat value of BLS(kJ/tonne pulp) increases. With the increase of dilution factor from 0 to 5, heat value of BLS increases nearly 6.314%, 4.09% and 4.446% for two, three and four stage washers respectively. It is also shown in figure if number of stages increased from 2 to 3 and 3 to 4 heating value increases of the order 2.07% and 0.806% respectively for a fixed dilution factor 2.5. With the increase in number of stages washing efficiency(solid removal) increases and as a result heating value increases. Hence, heating value of BLS is truly a function of dilution factor and number of washers.



5.4.7 Effect of Yield for Hardwood and Bamboo

Algorithm-1 is used to examine the effect of % yield of brown stock on heat value per tonne unbleached pulp, the same per kg of BLS and steam generation to the mill. The influence of yield is shown in Fig.5.9 and Fig.5.10. It is evident that with the decrease of yield from 50 to 40, increase of total heat value per tonne of unbleached pulp is of the order of 29.98%, decrease heat value per kg of BLS nearly 0.51% are noticed. These are expected behaviour.

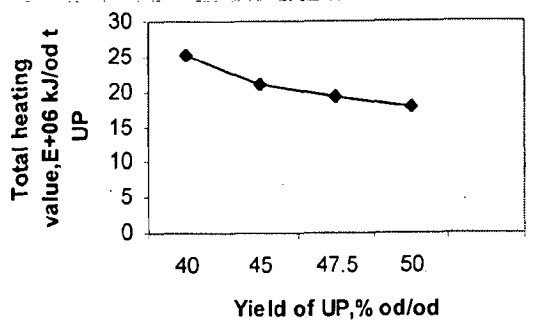


Fig.5.9 Effect of Yield on Total Heating value

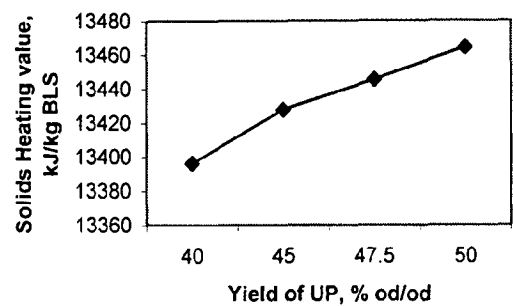


Fig.5.10 Effect of Yield on Solids Heating Value

5.5 DEVELOPMENT OF REGRESSION MODEL

The data generated are subjected to statistical multiple regression analysis using Mathcad software. The methodology and a typical set of data is given in APPENDIX-IX. The following equations are the results

$$HV = 5 \times 10^5 (DF) + 2.678 \times 10^5 (N) + 2.841 \times 10^7 \quad \text{with } R^2 = 0.87$$

$$\text{Steam to mill} = -16.92(DF \cdot N) - 31.407(N^2) + 344.195(N) + 6.093 \times 10^3 + 183.132(DF) - 14.481(D) \quad \text{with } R^2 = 0.96$$

This will be used for optimization of brown stock washer given in Chap-6.

5.6 CONCLUSIONS

Two algorithms(algorithm-1 and 2) are developed based on a modified form of Green and Grace procedure and computer programs using C++ language are developed to calculate heat value of black liquor solids and steam production from recovery furnace. The following conclusions can be drawn:

- With the increase of BLS there is slight enhancement of HV. Similarly ,if one intends to increase the number of stages increase of HV is noticed slightly.
- The sulphidity enhances the heating value with strong linear characteristics.
- The heating value of BLS rises with the increase of active alkali charge.
- Increase in percentage solids of black liquor will decrease the HV slightly. If one increases the number of stages of BSW ,the heat utilized for steam generation, will, however, increase.
- With the increase of thermal efficiency the heating value utilized to steam increase linearly. If one goes on adding the number of stages in BSW system, the heating value becomes higher and higher.
- Higher the dilution factor higher amount of lignin is available in BLS with an initial rapid change from DF from 0.0 to 2 and becomes almost constant thereafter. As expected , higher the stages more will be the lignin extracted, increasing its yield. As we go on increasing dilution factor, total black liquor solid t/t pulp will be increased. With the increase of number of stages at a fixed dilution factor BLS increases. There is no significant increase of BLS between dilution factor 2 to 4. But a rapid change in BLS to recovery is observed between DF 4 to 5.
- With the increase in dilution factor there will be an increase in heat value of BLS/tonne of pulp for all the stages, higher for the greater number of stages. If number of stages increased

heating value increases for a fixed dilution factor. With the increase in number of stages, washing efficiency (solid removal) increases and as a result heating value increases.

- Based on the data a regression model of nonlinear type is developed for further optimization.

STATISTICAL ANALYSIS AND OPTIMIZATION

6.0 INTRODUCTION

As already mentioned in Chap-1 that Pulp and Paper Industry has many mathematically complex subsystems such as multi stage digestion, brown stock washing, multi stage bleaching, multiple effect evaporation, mud-washing, recovery boiler operation, recausticizing, lime kiln and effluent treatment plant. Input and output parameters of each subsystem have an important impact on the operation of the entire pulp mill. For example, the input parameters for brown stock washing are: input consistency of pulp, dissolved solids with the pulp, temperature, number of washers and dilution factor etc. and output parameters are: outlet consistency of discharged pulp, outlet dissolved solids with the pulp, percentage solids to evaporator and displacement ratio etc.. Change in percentage solids to evaporator (feed Concentration) is resulted due to change in dilution factor which will affect the steam consumption, steam economy and area requirement for evaporator operation. Similarly, dilution factor has an effect on solids out with discharged pulp and its outlet consistency. These output parameters of BSW will also affect the chemical consumption and values of effluent parameters generated from bleach plant. Therefore, dilution factor (DF) and number of stages (N) of BSW have a visible impact on other subsystems. For a fixed set of output parameters for each subsystem an optimum DF and N are required to estimate. For this purpose, functional relationship among output parameters, DF and N should be known. But this is a mathematical programming problem on multiple effect evaporator of black liquor coupled with brown stock washer and bleach plant is reported till today. In this present study, mathematical and statistical tools are employed for optimization study. By using regression analysis the functional relationships are obtained among the variables and are then subjected to optimization of BSW. The

objective of present work is to study the effect of DF and N on various output parameters of the above operations and more importantly, to find appropriate models (statistical or mathematical) that could be used to predict the dependent variables (steam, power and chemical consumption, heat value of BLS etc.) at various values of DF and N. Finally the optimized values of them need to be evaluated through constrained nonlinear optimization and to be checked via graphical optimization.

Before running all possible regressions, one must consider what criteria should be used to select the best fitting equation from all possible regressions. Among the various criteria for selecting the best regression equation from the set of all possibilities, the coefficient of determination R^2 criterion and Mallows' C_p criterion are available for selecting independent variables. By examining the models that have the highest R^2 values, one can identify the number of pertinent variables to include in the model. In addition, the residuals (actual values – predicted values) of these models are to be plotted with respect to predicted values. All of the residuals must scatter around zero and are independent of the predicted values. If the sum of residuals is zero, then it is the required best fitting equation. In this chapter a brief review of all the relevant models developed in different chapters are reproduced with a view to get a glimpse of optimization methodology for brown stock washing of pulp. Objective function of brown stock washing from Chap-1, capital and fixed charges together with power cost of BSW from Chap-2, statistical multivariate regression model from Chap-3 for steam and condensate flow, carry over of solids and neutralization cost in bleaching operations from Chap-4 and heat value of lignin and its impact on overall gain in the recovery furnace from Chap-5 are incorporated. The above parameters are converted in terms of cost as required in Eq.1.5 of Chap-1 and then subjected to nonlinear constraint optimization by Fletcher-Reeves method. These are described in brief as under.

6.1 DEVELOPMENT OF MODELS FOR MULTI-STAGE BROWN STOCK WASHING

The mathematical models are attempted as indicated above for multi-stage washing plant, multi-effect evaporator, multi-stage bleaching plant and finally, heating value of black liquor solids calculations and the effect on steam generation.

6.1.1 Objective Function (from Chap-1)

The objective function of multi-stage brown stock washer can be formulated as follows:

Total cost of washing (C_T) = Cost of washing Equipment (P_w) + Cost of maintenance repair (P_m) + Cost of power due to drum rotation, back shower pump, vacuum pump, ($P_o * C_{13}$) + Cost of power for repulper-shredder ($P_o * C_5$) + Cost of power due to liquor spray ($P_o * C_6$) + cost of power for screw conveyer at last BSW ($P_o * C_4$) + Labour cost (C_{LW}) + Cost of steam for hot water ($P_A * C_A$) + Cost of evaporation ($P_E * C_E$) + Cost of steam generated due to heat value of BLS ($P_E * C_L$) + Cost of condensate saving ($P_s * C_s$) + Cost of bleach chemicals due to carry over solids ($P_{NB} * C_{NB}$) + Cost of effluent treatment ($P_{Eff} * C_{Eff}$) + Cost due to soda loss ($C_{sl} * P_{sl}$) + Cost due to total solid loss ($C_{tsl} * P_{tsl}$)

$$\text{Min } (C_T) = (P_w + P_m) * N + P_E * (C_E + C_A + C_L) + P_s * C_s + P_{NB} * C_{NB} + (C_{13} * N + C_5 * (N-1) + C_6 * N + C_4) * P_o + C_{LW} + P_{Eff} * C_{Eff} + C_{sl} * P_{sl} + C_{tsl} * P_{tsl} \quad (6)$$

Where C_{13} = power consumption due to drum rotation (C_1) + back shower pump (C_2) + vacuum pump (C_3). The cost of production of steam is actually a benefit like the saving in condensate. In optimization these are added in the total cost of BSW as shown by Gerald (43).

6.2 MODELING OF MULTIPLE EFFECT EVAPORATOR FOR BLACK LIQUOR CONCENTRATION (from Chap-3)

The modeling of multiple effect evaporator necessitates the first hand information of the optimum number of effects in a multiple effect evaporator set-up for a particular process industry based

prevailing costs. This, in turn, will be used to develop a system of non-linear algebraic equations depending upon number of evaporator bodies in MEE which is elaborated in Chap-3.

6.2.1 Annual Cost Model for Optimal Number of Effects

For evaluating steam and condensate saving, the required step is to develop an approximate annual cost of evaporation as a single valued function of number of effects(N) for which an objective function has been formulated as follows(from Chap-3 Section 3.3.1):

Total cost of evaporation(C_e)=Cost of labour(C_L)+Supervision charges(C_{SL})+Cost of overall laboratory, administrative(C_{OLA})+Fixed charges(C_{fc})+Cost of cooling water(C_{cw})+Cost of steam(C_s)+Periodic cleaning cost(C_c)+Cost of maintenance and repair(C_{mr})+Cost of air handling equipment(C_{ae})+Cost of equipment for condensing, injection(C_{ce})+Cost of loss of capacity due to BPR(C_{BPR})

$$C_e = \text{Min} (C_L + C_{SL} + C_{OLA} + C_{fc} + C_{cw} + C_s + C_c + C_{mr} + C_{ae} + C_{ce} + C_{bpr})$$

Based on prevailing cost of equipments and utilities it has been found that the optimum number of effects is six(details in Chap-3 Section 3.3.3).

6.2.2 Models of Nth Effect Evaporator System

For the solution of sextuple effect evaporator one needs the selection of appropriate correlations of physico-chemical / thermal and transport properties as a function of temperature and solid concentration, development of steady state material balance, heat balance, rate equation for a particular set of multiple effect evaporators and also the overall heat transfer coefficient.

In this present investigation climbing film long tube evaporator set of six bodies for wood/bamboo based black liquor is used. The Newton- Raphson-Jacobian matrix and Gauss Elimination are employed to solve a set of 12 non-linear simultaneous algebraic equations resulting from the multiple effect evaporator model. Computer program based on Fortran-77 has been developed to generate data on steam consumption, steam economy and area requirement for various values of

dilution factor(DF), and number of stages(N). These are subjected to multivariate nonli regression equation for the BSW optimization.

6.3 MODELING AND OPTIMIZATION OF A MULTI-STAGE BLEACH PLANT(f Chap-4)

For the optimization of washing plant bleach plant needs to be optimized. In order to fulfil the an objective function to minimize the cost of bleach plant in terms of bleaching chemicals, steam consumption has been formulated for a specific target variable (brightness in this case) kappa number as follows:

Total annual cost of bleaching(Z)=Base cost(C_0)+Cost of Chemical Consumption in stage 1 $2(C_1*x_1)$ +Cost of chemical consumption in stage3(C_2*x_3)+Cost of chemical consumption in s 4 and 5(C_3*x_5)+Cost of steam in stage 1 and 2(C_4*y_1)+ Cost of steam in stage 1 and 2(C_5* Cost of steam in stage 1 and 2(C_6*y_5).

$$Z=C_0+ C_1x_1+ C_2x_3+ C_3x_5+ C_4y_1+ C_5y_3+ C_6y_5$$

Linear programming with constraints has been used to solve the problem with CEDED bleacl sequence as an example. The equations for estimating the neutralization cost due to consump of NaOH is shown in Table 6.1.

6.3.1 Development of Statistical Multi-variate Models for Pollutants in Bleach Plant Estimate Pollutant Parameters

Multiple regression equations are also developed to estimate the effluent parameter(i.e.At COD, BOD,TOCl, color etc.) and their inter-relationships from the chemical consumption du either kappa number, carry-over solids or both from BSW. The total impact of effluent genera on BSW has been quantified using these inter-relationships and with BOD₅ or COD or AOX ; major variable which have been shown as a function of DF and N. These are also depicted Table-6.1.

6.4 MODELS FOR HEATING VALUE OF BLS(from Chap-5)

Algorithm-2 of Chap-5 is used to obtain the heating value of BLS for various DF and number of stages of washers. The relationship between steam generation due to heat value of BLS, DF and N is obtained by using multivariate nonlinear regression analysis.

6.5 METHODOLOGY FOR STATISTICAL ANALYSIS OF DATA

It is a fact that when the model is appropriate, points must be the nearest possible from the diagonal. Explicitly, this type of representation gives more information than just reporting regression coefficient R^2 values. If points are randomly distributed above and below the diagonal line the values of dependent variables are accurately predicted. If not, it is difficult to explain by any type of correlation available in literature. The values of residuals are also plotted to confirm more clearly against estimated (predicted) values, which must indicate that, for each dependent variable, residuals should be randomly scattered. If both the statistical tools give the accurate predictions, the multiple linear and nonlinear regression models are satisfied.

In this present study, three well known statistical methods are used, namely, plotting predicted vs experiment/ treated data ,multiple regression coefficient, R^2 , and the residual plot for checking the validity and accuracy of the statistical models. The data obtained from different mathematical models are subjected to single /multivariate statistical linear or nonlinear regression models. The variables are either N, DF or both for representative equations in optimization program of BSW plant. Some of the statistical models are shown in Table-6.1. The methodology for obtaining the single variable or multi-variate linear or non-linear regression are given in APPENDIX-III For obtaining quick program Mathcad software is used.

Using the relevant algorithms and computer programs based on C ++ language, the values of total solid loss, total soda loss and percentage solid to evaporator and the relevant correlations are obtained.

Table-6.1 Regression Equations

Parameters	Regression Equation and their Nature	R ²
Steam to evaporator	$3.66 \cdot 10^{-3}(DF \cdot N) + 5.39 \cdot 10^{-3}(N^2) - .054(N) + 2.43 + 0.073(DF) - 2.207 \cdot 10^{-3}(DF^2)$ <ul style="list-style-type: none"> • Multivariate nonlinear regression 	0.999
Steam to mill	$-16.92(DF \cdot N) - 31.407(N^2) + 344.195(N) + 6.093 \cdot 10^3 + 183.132(DF) - 14.481(DF^2)$ <ul style="list-style-type: none"> • Multivariate nonlinear regression 	0.96
ΔS	$-22.346(DF \cdot N) - 50.303(N^2) + 520.644(N) + 1.059 \cdot 10^3 + 260.227(DF) - 21.57(DF^2)$ <ul style="list-style-type: none"> • Multivariate nonlinear regression 	0.96
NaOH consumption	$5.462(DF \cdot N) + 8.486(N^2) - 84.829 \cdot N + 303.601 - 76.038(DF) + 7.197(DF^2)$ <ul style="list-style-type: none"> • Multivariate nonlinear regression 	0.988
Soda loss	$4.25(DF \cdot N) + 6.593(N^2) - 65.947 \cdot N + 236.164 - 59.176(DF) + 5.602(DF^2)$ <ul style="list-style-type: none"> • Multivariate nonlinear regression 	0.98
Hot wash water	$303.67 + 57.84(DF) - 2.33 \cdot 10^{-4}(DF^2)$ Single variable parabolic regression	1
Power consumption	$P_2 = 0.243 + 2.69 \cdot 10^{-3}(DF) + 3.78 \cdot 10^{-5}(DF^2)$ <ul style="list-style-type: none"> • Single variable parabolic regression 	1
BOD	$2.635(DF \cdot N) + 3.222(N^2) - 32.987 \cdot N + 145.13 - 30.819(DF) + 2.926(DF^2)$	0.975
AOX	$0.451(DF \cdot N) + 0.695(N^2) - 6.969 \cdot N + 29.837 - 6.29(DF) + 0.596(DF^2)$	0.988

6.6 COST DUE TO EFFLUENTS TREATMENT

The treatment of effluents involve considerable capital and operational costs. In brown stock optimization the contribution of this cost is to be examined. A preliminary attempt is being made in this investigation to estimate atleast an approximate value of this parameter. Accurate value can be obtained if detailed accounts of pulp types, raw materials, washing practices, bleaching sequence, and specially the ETP configurations (pre, primary, secondary and tertiary treatment , aerobic/ anerobic or combination) are known. Therefore, it is extremely difficult to precisely find out the total treatment cost including fixed charges due to capital investment for equipments for a greenfield mill or a mill under operation. However, an order of estimate figures can be worked out based on published information.

Mccubbin and Folke(68) indicated that 84 US \$ per kg of AOX or an equivalent 120 US \$ per tonne of bleached pulp (for reduction of 1.5 kg AOX) is required. This includes operating cost and annualized capital costs. However, the initial and final values of AOX were on the order of 1.8 kg and 0.3 kg/t respectively. The low value of AOX (1.8kg/t) might be due to pre-oxygenated bleached sequence with oxygen-peroxide reinforced extraction. In Indian practice with CEDED sequence, the AOX entering to ETP will be much higher. The expenditure might be prohibitively high. Gullischen(35) has also reported regarding the effect of some delignification methods on the properties of untreated effluents from a softwood Kraft bleach plant with initial BOD₇ of 16 kg/t ,COD 80 kg/t and AOX 7kg/t. For standard Kraft, the effluent quality after activated sludge treatment has been considered 2.4 kg/t, 55 kg/t,and 3.9kg/t respectively for BOD₇.,COD and AOX. The cost of reducing the total load of BOD to 5%, COD to 25%,color to 12% and AOX to less than 10% of that released from a standard Kraft mill without effluent treatment would be less than 4% of the product value. Report is also available regarding the estimated cost for BOD₇ reduction to 9 kg/t₉₀ pulp for conventional bleaching sequence as 0.32 US\$ per kg of BOD₇ and

0.06 US \$ per kg of COD(from 90kg/t to 41 kg/t). This cost after adding fixed charges assumed 50% of the total cost (5% of the fixed capital investment) based on Liebergott et al.(61) for activated sludge treatment per tonne of pulp amounts to approximately Rs 306.7 per ton (assuming 1 US\$=45 Rupees) based on BOD and 293.3 rupees based on COD for Indian conditions. It has also been reported(56) that expenditure on the order of Rs.1 is required for 1 BOD removed for an Indian mill. Using escalating factor of 1.2 and the value of money of years period the cost per kg of BOD removed is on the order of 6.19 Rs. to meet pollution control norms which is equivalent to Rs 324.6 per tonne inclusive fixed charges In all the above calculations the BOD₅ of 30ppm and 200 m³ per tonne of waste water discharge are assumed . The operational cost for effluent treatment in a typical paper mill of 300 TPD to adhere to regulatory norms by Central Pollution Control Board, can be estimated indirectly through power consumption in aerators if the system configuration for the effluent treatment involves aeration system. From actual plant study in India it has been found that the total operational cost is approximately three times of the power consumption by the motor of the aerators. It is experienced that nearly 21 aerators each of 40hp are required for the above mill. From this it is evident that for a 24 hour a day the total electrical energy consumption is of the order 15120kWh. On per tonne basis and considering Rs.3-4 per unit the operational charges are approximately 151.2 to 201.6 Rs./t. If one takes into account of fixed charges the same can be estimated on the order of Rs. 302.4-403.2/t.

It is very interesting to note that in all cost estimation procedures cited above (directly or indirectly) the treatment costs are found on the same order. Therefore, this data can be conveniently used for optimization purpose.

The calculated cost based on BOD is surprisingly found to be very low in comparison if one calculates based on cost figure of AOX removal. In India AOX has not found any place in nor

of pollution control authority till now. However, TOCI has prescribed value of 2 kg/t. Therefore, the cost of effluent treatment due to AOX can be indirectly estimated through TOCI value, though there is little difference between the two parameters. This is just to examine the impact of AOX on optimization as a comparison. On the otherhand, calculation through BOD₅ or COD is more reliable.

An attempt will be made to examine the effects of these costs to get optimum parameters of BSW in the following section.

After obtaining all the relevant terms as demanded by Eq.1.5 of Chap-1 the process of optimization is accomplished as under:

6.7 OPTIMIZATION OF BROWN STOCK WASHERS

The optimization of multi-stage BSW is a non-linear programming problem with constraints. Conjugate Gradient(Fletcher-Reeves) method of constrained optimization is used to solve the present problem. The details of this method is described in APPENDIX-V.

6.8. RESULTS AND DISCUSSIONS

Based on the plethora of data generated, the interpretations are made with graphical plots. In this present investigation, the dependent variables were soda loss, sodium hydroxide consumption, steam consumption in MEE operation, heat value of BLS and steam generated by combustion of BLS in recovery furnace.

6.8.1 Interpretation of statistical Regression Models for various parameters for optimization

Results are drawn in various plots to verify the accuracy of the model.

Figs.6.1 through 6.3 6.5, 6.7 and 6.9 provide a visual way to calculate the goodness of fit for the multivariate linear and nonlinear regression models developed through statistical analysis. It consists of plotting the predicted values of various parameters resulting from the mathematical regression equations indicated in the graphs as a function of experimental/extrapolated or

regression equations indicated in the graphs as a function of experimental/extrapolated interpolated data or data obtained from the algorithm developed.

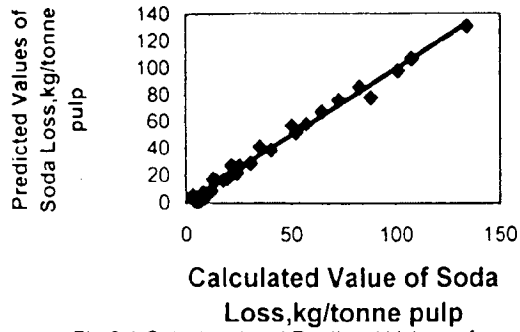


Fig-6.1 Calculated and Predicted Values of Soda Loss

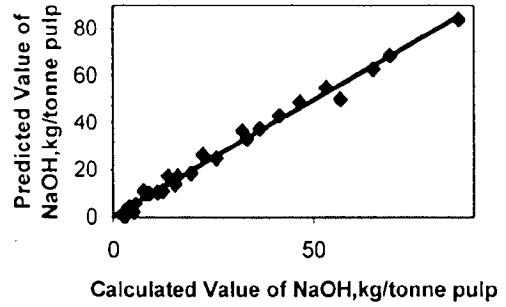


Fig-6.3 Calculated and Predicted Values of NaOH

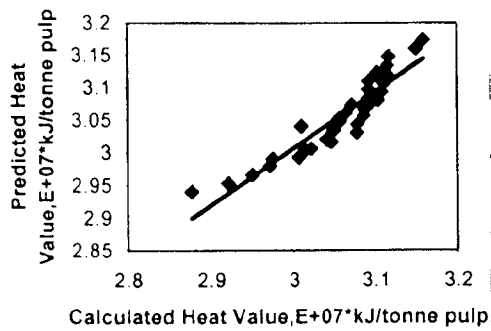


Fig-6.5 Calculated and Predicted Values of Heat Value of Black Liquor Solids

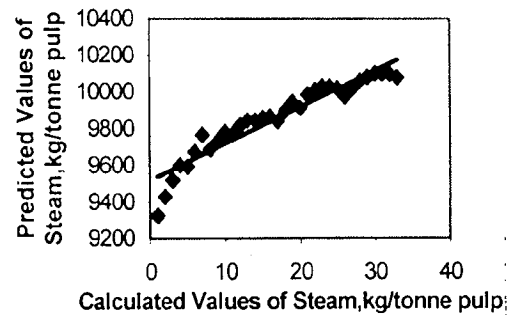


Fig-6.7 Calculated and Predicted Values of Steam to Mill

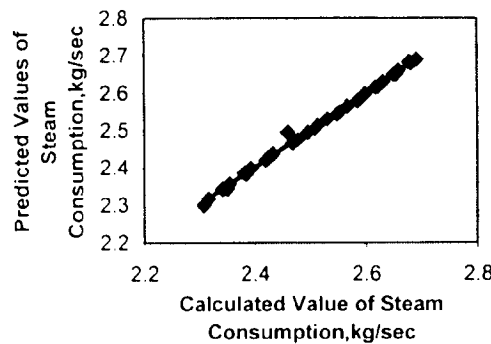


Fig-6.9 Calculated and Predicted Values of Steam Consumption (Evaporator)

igs.6.2, 6.4, 6.6, 6.8, 6.10 are the plots of residuals Vs predicted values.

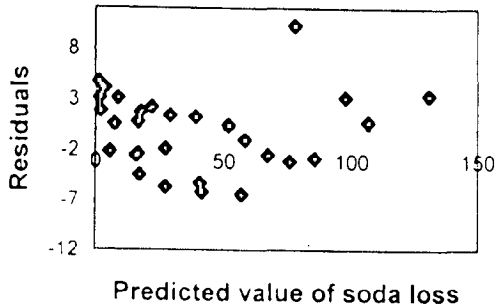


Fig.6.2 Residuals vs Predicted value of soda loss

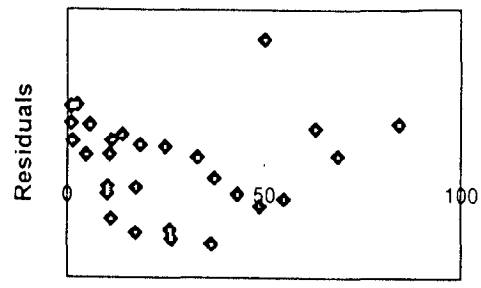


Fig.6.4 Residuals Vs Predicted value of NaOH consumption

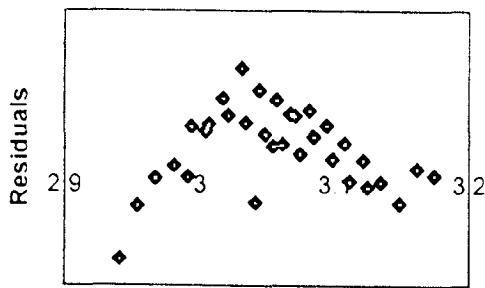


Fig 6.6 Residuals vs predicted value of Heat value of BLS

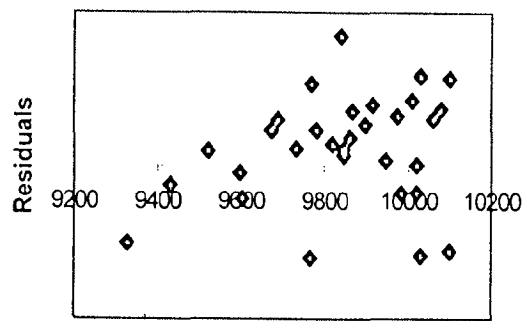


Fig.6.8 Residuals vs predicted value of steam to mill

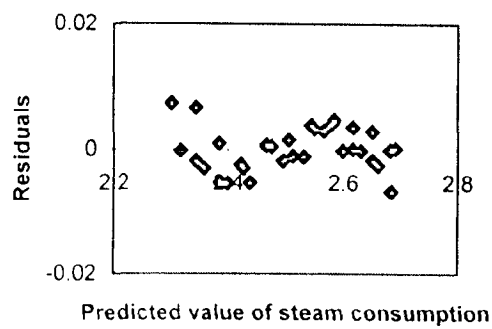


Fig 6.10 Residuals vs Predicted value

In Figs. 6.1, 6.3, 6.9 the data predicted from statistical model Vs calculated based on algorithm are plotted. It is evident from the figures that there is a very good agreement with each other.

From Figs 6.5 and 6.7- the plots for black liquor solids and steam generated through combustion of BLS in recovery furnace, it is also reflected that the results are also quite satisfactory but with slightly lesser accuracy and reproducibility compared to the those from Figs. 6.1, 6.3, 6.9. The residual plots also behave in the same manner. The values of R^2 , the multiple correlation coefficient also support the above findings. This is clearly shown in Table 6.1.

From the statistical analysis of data it is very much clear that they act as better indicators than the existing models. Therefore, the analysis and design of the above system can be accomplished with the developed regression models without any appreciable error. The magnitude of the error which are insignificant, can be permitted to ignore for process design calculations. It is also found that the models, both statistical as well as the algorithm based on static/steady state model can reasonably be used for engineering design estimates within its range of applicability.

6.8.2 Interpretation of the Results of Nonlinear Optimization with constraints through Fletcher Reeves method.

The general solution techniques for optimization are depicted in details in APPENDIX-V From the results of constrained nonlinear optimization, it is found that the dilution factor(DF) and number of stages(N) are of the order of 2.789 and 3.958(≈ 4 as N can not be a fraction) respectively for minimum cost of washing. This result is based on total annual cost taking in to account all costs including BOD treatment cost. As with usual convention, in this treatment, BOD₅ has been taken as effluent parameter.

Cost of Evaporation, condensate saving and steam generation due to BLS are found to be the major contributors to the total cost. All other factors have only the minor share to the total cost.

optimization of washing operation. The relative contribution of each factors are shown in the following Table 6.2.

Table 6.2 Relative contributions of all cost contributing parameters(on % basis)

C_e	C_{CS}	C_{hw}	C_{NaOH}	C_{Sl}	C_{eff}	C_{sm}	C_{eq}	C_p	C_{pl}
21.244	8.497	3.79	0.967	0.6845	3.559	60.067	0.353	0.05079	0.777

From the Table the following concluding remarks can be made regarding the relative contribution of various costs towards total cost in ascending order :

$$C_p > C_{eq} > C_{sl} > C_{pl} > C_{NaOH} > C_{eff} > C_{hw} > C_{cs} > C_e > C_{sm}$$

If cost for effluent parameter is neglected the optimum results are found to be of the order of DF=3.24 and N=3.83. On the other hand, if one does not consider the term steam to mill and condensate saving at all, the optimum values of DF and N become 3.66 and 3.77(≈ 4) respectively. The optimum results for DF and N yield the respective values 3.67 and 3.79(≈ 4) if effluent parameter due to BOD₅, steam production and condensate saving are not considered. The results also indicate that there is drastic enhancement of values of at least DF if one neglects (i) BOD(+13.91%), (ii) steam to mill and condensate saving(+23.79%),(iii) BOD, steam to mill and condensate saving(+24%).

In actual practice, this benefit accrued due to steam saving caused by black liquor solids in terms of cost can also be treated as difference between present study and those from some base value of a standard mill and thereafter optimization should be carried out based on this difference expressed as a function of DF and N. For the later, another regression equation has been developed as shown in Table 6.1. The optimized results based on this new program are found to be on the order of DF=2.5 and N=4.19(≈ 4). Therefore, it is clear that there is a slight decrease of DF values ($\sim 10\%$) and increase of N values($\sim 5.02\%$). Comparison of results reveals that though there are

significant contributions of each of the above costs towards the total annual cost, these are sensitive to the optimum values, namely DF and N. Probably this is the reason, many previous workers overlook^{ed} their inclusion in their optimization scheme. Impact of AOX is not considered in the analytical optimization as it is not the usual parameter in sharp contrast to BOD. Once the results are obtained it is customary to examine through graph as most of earlier results are explained through graphical construction.

6.8.3 Graphical Interpretation of data from Cost Equation for Optimizing Parameters

The overall annual cost equation, Eq. 6.1 is subjected to various values of DF and N. All individual cost components as a functional dependence on DF and N are also estimated. Two cases have been considered for effluent treatment cost- one with AOX and the other with BOD₅. AOX has been considered just to examine the validity of cost reported by one investigator (68). However no stresses have been given on estimating effluent treatment cost based on BOD₅, as except one investigator recommended this parameter. This is mainly because both on-line as well as off-line BOD values from a plant are easily and reliably determined compared to any other parameter such as AOX, COD etc.. The cost terms are now plotted in figures to see the effects of DF and N in order to find out optimum values. In this optimization scheme, cost benefit due to ΔS , difference of steam production from a standard base is not considered as it is evident from

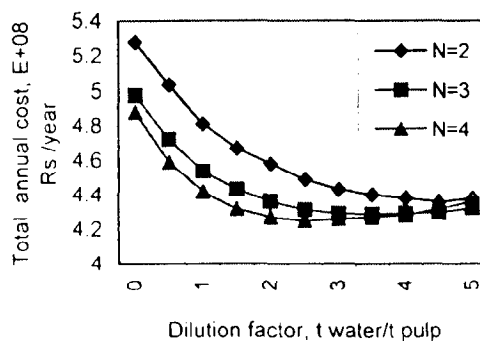
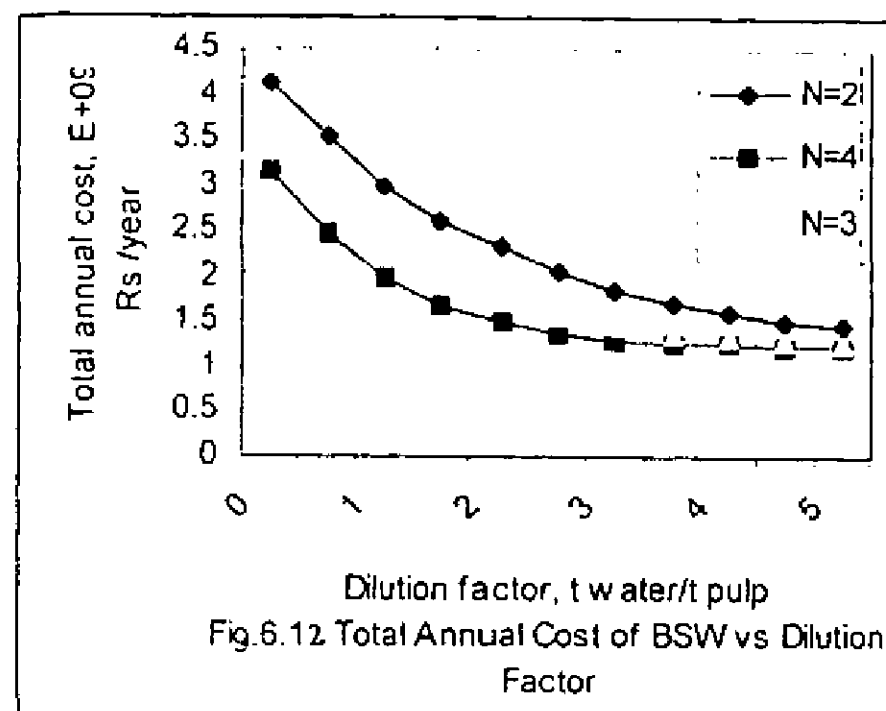


Fig 6.11 Total Annual Cost of BSW vs. Dilution Factor

analytical optimization that it has no impact on the optimized values. Fig.6.11 shows the variation of total annual cost of BSW for various DF and N, if one considers treatment cost for BOD.

If one takes in to account the cost for AOX treatment as parameter in ETP, the total annual cost of BSW for various dilution factor and number of stages are depicted in the Fig.6.12. It is evident



from the figure that if one considers the AOX treatment cost the DF and N become 4.5 and 4 respectively. The higher value of DF obtained in this case is due to very high value cost considered (68) in the optimization scheme. In fact, the AOX treatment cost reported by Maccubin(68) is far beyond the stipulated value on product basis(4%) advocated by Gulichsen(35).

If one neglects the cost of effluent treatment the effect of dilution factor on total annual cost can be shown in Fig.6.13. Neglecting the cost of AOX treatment while the N remains the same, DF comes down to 2.5. It indicates that the AOX treatment cost has significant influence on the optimized parameters of DF. On the other hand, it is also reflected that there is negligible impact on the value of N. As expected the value remains the same if one neglects the BOD treatment cost from the cost equation.

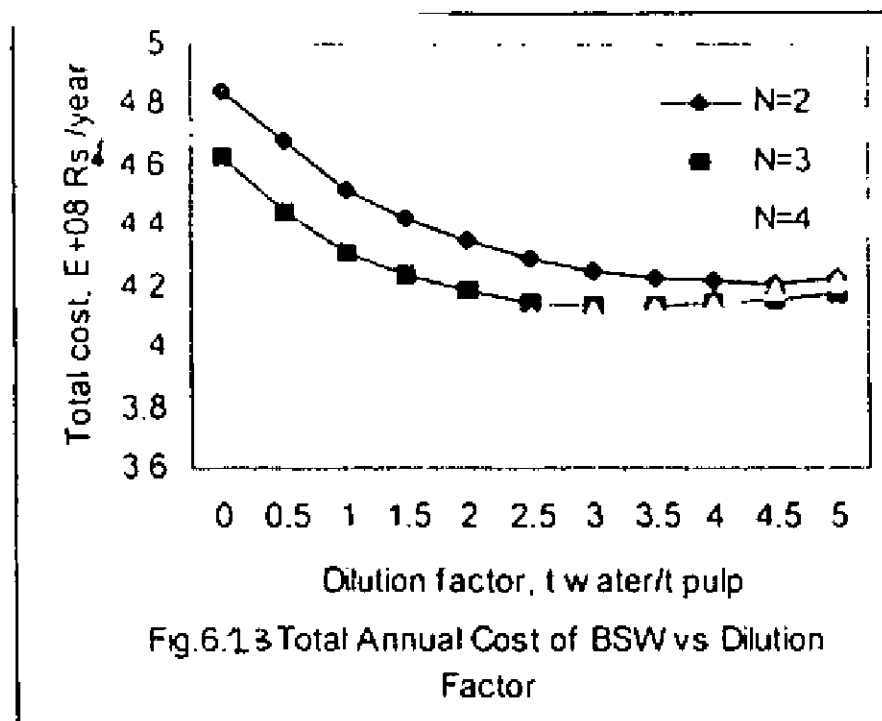
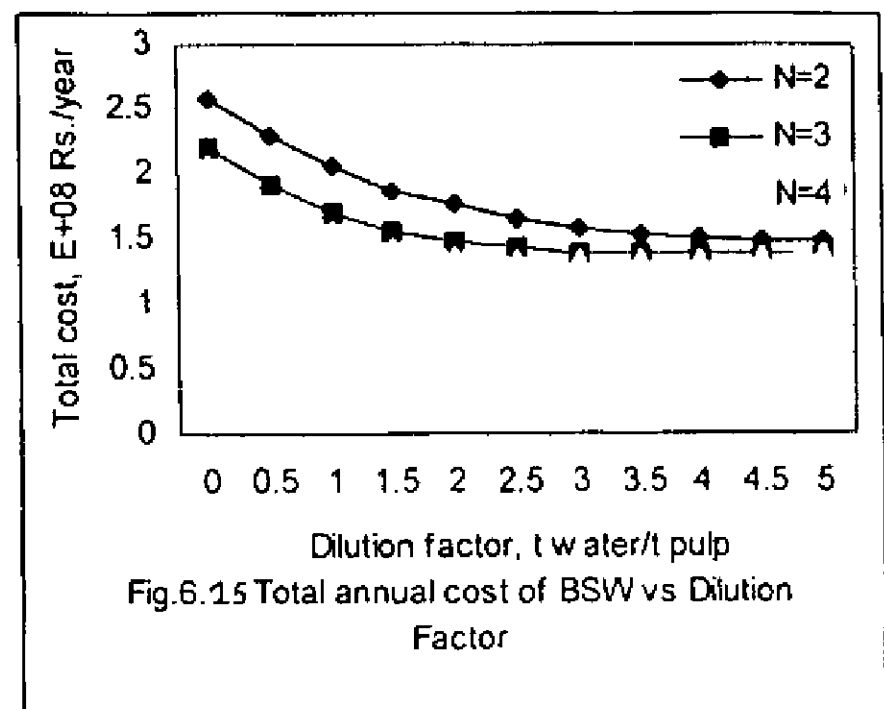
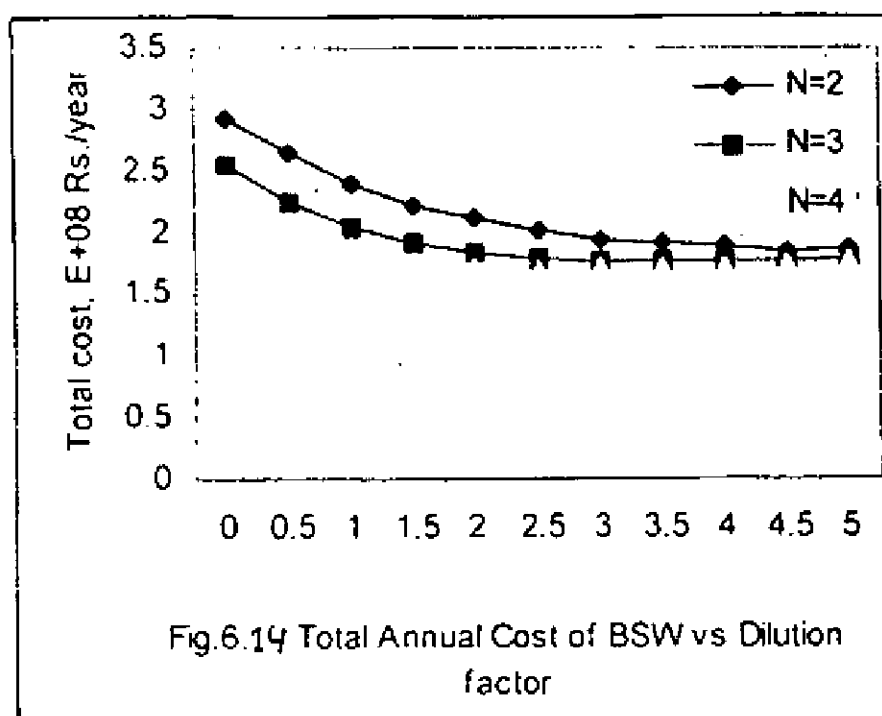


Fig. 6.14 and Fig. 6.15 have been plotted with total annual cost of BSW as a function of dilution



factor for different number of stages. It is evident from the figure that without considering the gain due to steam generation (Fig. 6.14) and condensate (Fig. 6.15), the values of optimum parameters i.e. DF and N are 3.0 and 4 respectively for BOD consideration. From the figures it can be concluded that though the cost of steam generation and condensate saving are high it bears no significant effect on optimized values. The optimized value from the mathematical optimization gives slightly higher value than that visually observed from the graphs. This is true for both the cases namely considering BOD and AOX. It is very interesting to note that neglecting BOD (or AOX) or neglecting steam generation benefits term yields the same result. If both are neglected the DF and

N stand on the order of 2.5 and 4. Therefore, optimum number of values obtained from graphs are insensitive of the aforesaid parameters. The results of both analytical optimization and graphical procedures for various cases are compared in Table-6.3.

Table-6.3 Comparison of results from Analytical and Graphical Optimization

Parameter	Graphical optimization		Analytical optimization	
	DF	N	DF	N
Including BOD	2.5	4	2.789	3.958
Δ steam production	-	-	2.5	4.19
Including AOX	4.5	4	-	-
Excluding effluent parameters	2.5	4	3.24	3.83
Excluding steam production and condensate saving	3.0	4	3.66	3.77
Excluding steam production, condensate saving and effluent parameter	2.5	4	3.67	3.79

The optimized value from the mathematical optimization gives slightly higher value than that visually observed from graphical optimization. Neglecting BOD (or AOX) or neglecting steam generation benefits term yields the same result in graphical optimization. If both are neglected the DF and N stand on the order of 2.5 and 4. Therefore, optimum number of values of DF and N obtained from graphs are insensitive of the aforesaid parameters. These values are in close

agreement with the values obtained from nonlinear constrained optimization considering all the costs. Therefore, the DF between 2.5-2.8 and number of stages of 4 can be taken as optimum values.

6.9 CONCLUSIONS

Based on the models and algorithm developed on the physical problems relating to washing and bleaching of pulp, evaporation of black liquor and black liquor heating value and their interaction the following conclusions can be drawn.

- Soda loss, total solid loss, percentage solid to evaporator, chemical consumption in bleach plant decrease with the increase in dilution factor. Soda loss, total solid loss, chemical consumption in bleach plant decrease with the increase in number of stages at any given dilution factor. Steam consumption for hot wash water, power consumption due to liquor spray increase with the increase in dilution factor. This is in close agreement with those from the previous investigators.
- Model developed can predict data for the performance of evaporator very well. Newton-Raphson-Jacobian matrix and Gauss Elimination thus can be used for rapid convergence. With the increase of dilution factor steam consumption to evaporator and condensate saving increase. With the increase of number of stages percentage solid to evaporator increases and hence steam consumption and condensate saving decrease for any given dilution factor. The multivariate nonlinear regression equation predict the steam consumption very well for a given dilution factor and number of stages.
- From the bleach plant studies, it is found that linear programming technique can be used for complete optimization of bleach plant. The procedure developed by Freedman(23) is modified in this present work for bleach plant optimization. This scheme of optimization can boost a significant economy by saving chemicals and steam. Saving on the order of Rs. 300 per ton

of bleached pulp can be anticipated which is substantial if considered annually. The multivariate statistical regression equations for estimating environmental parameters like AOX, COD, BOD etc. are found to be better fitted than the existing correlations. Thus they can predict more accurate values of environmental load on the bleach plant and hence indicate better financial estimates for the bleach plant. Neutralization cost, suggested by Shackford(97) can equally be applicable here for both kappa number and carry over solids variation.

- The model developed for heat value is an extension of Green and Grace(32) model and can be used safely to estimate the impact of washing on black liquor solids heating value. Black liquor solids heating value and steam generation due to this increases with the increase in dilution factor and number of washers.
- From the results of constrained nonlinear optimization of washing operation based on total annual cost taking in to account all costs including BOD treatment cost, it is found that the dilution factor(DF) and number of stages(N) are of the order of 2.789 and 3.958(≈ 4 as N can not be a fraction) respectively for minimum cost of washing. The results also indicate that there is drastic enhancement of values of at-least DF if one neglects (i) BOD(+13.91%), (ii) steam to mill and condensate saving(+23.79%),(iii) BOD, steam to mill and condensate saving(+24%). The number of stages become almost insensitive for the with-drawl of above cost items from the total annual cost equation.
- Cost of Evaporation, condensate saving and steam generation due to BLS are found to be the major contributors to the total cost. All other factors have only the minor contribution to the total cost for optimization of washing operation. Though the cost of steam generation and condensate saving are high it has no significant effect on optimized values.
- AOX based cost consideration gives much higher value of DF than if one considers cost due to BOD treatment in the total cost equation. This is probably due to high cost reported by

Macubbin(68). This seems unrealistic as it does not match with the stipulated value indicated by Gullichsen(4% of product value). On the other-hand, cost due to BOD₅ treatment remains on the same order of magnitude if one calculates on the basis of both published data as well as from those from practice.

- The optimized value from the mathematical optimization gives slightly higher value than the visually observed from graphical optimization. Neglecting BOD (or AOX) or neglecting stage generation benefits term yields the same result in graphical optimization scheme. If both are neglected the DF and N stand on the order of 2.5 and 4. Therefore, optimum number of value of DF and N obtained from graphs are insensitive of the aforesaid parameters. These values are in close agreement with the values obtained from nonlinear constrained optimization considering all the costs. Therefore, the DF between 2.5-2.8 and number of stages of 4 can be taken as optimum values.

Chapter-7

RECOMMENDATION

This present investigation has been attempted as a prototype to illustrate the methodology in c to find out the optimum dilution factor for sending recommendation regarding set points control algorithm. However, the cost are assumed based on current practice in Indian mill. Tin time the true cost of various inventory can be simulated taking care of inflation and escal price index. However, this would give operations with a continuous indicator of cost which w provide a tool to minimize operating cost. The developed models can also be used for simul in determining fault diagnosis and undesirable process operation and aid in trouble shoc measures.

As a result of present investigation the following points are emerged out for future studies:

1. Experiment needs to be carried out to find out DR for different number of stages of BSW accurate estimation of parameters for evaporator and bleach plant, particularly soda loss, COD loss. Comparison should also be made with EDR and modified Norden efficiency fa values for deriving a globally acceptance criteria for the basis of optimization.
2. Modern methods of solution of MEE operation using artificial neural networks(ANN) Quasi-Newton method may be attempted to compare the computer time requirements and ascertain the accuracy of the later if any.
3. Evaporator should be optimized with mixed feed falling film configuration or PFR with possible economy measures like utilization of condensate and product flash in order to red both electrical and thermal energy consumption.
4. Dynamic programming should be attempted to optimize the evaporator parameters.

5. The splitting of bodies in MEE leads to more economy and also higher evaporation capacities. As regards bleeding, it further enhances the steam economy. Hence, various alternative schemes for split bodies vapour use and bleed point locations should be studied to evaluate their impact on capacity and steam economy of evaporators. Keeping the above in view it is obvious that both splitting and bleeding should also be considered along with other important parameters for the determination of optimum processing of black liquor.
6. The recent trend in the design evaporator is to use unequal heating surface areas in evaporator bodies. Therefore it will be of importance to consider this aspects for concentration of black liquor in MEE.
7. Boiling point rise data for different counts should be critically examined. BPR due to dissolved solids in black liquor should be evaluated in laboratory at various concentrations, pressures and vaccuum and different pulping conditions. The other parts of total BPR i.e. due to hydrostatic head and those due to dynamic heads(friction and kinetic) should be accurately monitored from an industrial scale of evaporator having different number of bodies. Thus the total BPR should be considered for optimal design of evaporators meant for different black liquor using various Indian raw materials(non woods and woods).
8. Effect of varying kappa number of pulp and the carry over solids should be accurately monitored in industry for different washing conditions of BSW as well as for various raw materials used in Indian industry.
9. The laboratory based experiment should be carried out to establish the relation among AOX, BOD, COD, soda loss and TOCl for various bleaching sequences like CEH, ECF with various chlorine di oxide substitution and also for TCF bleaching sequence.
10. Detailed study on the modeling of black liquor heating value based on experimental measurements of different Indian pulp mill liquors from varieties of raw materials and their

blends followed by simulation needs careful attention. The elemental composition of the black liquor solids, smelts, particulates, fumes and flue gases from a pilot recovery furnace required to be precisely evaluated in laboratory.

11. The effluent treatment cost must include the treatment configuration(pre-,primary, biological and secondary) including equipment parameters.
12. Consideration of aerobic, anaerobic or combination treatment and their effect on optimization should be examined.
13. Neutralization cost and cost of nutrients along with amortization of capital inventory and value of money can be added to the determination of cost in ETP.
14. The effect of sulphur loss in optimizing brown stock washer requires attention.

APPENDICES

APPENDIX-I

Algorithm for computation of solid reduction ratio for any number of stages in a multis washer

Step-1 Calculation of ratio of undiluted blow liquor to liquor in sheet liquor from washer

$$R_b = W_b/W_p = [(1-C_{yb})/C_{yb}] / [(1-C_{yp})/C_{yp}]$$

Step-2 Calculation of ratio of liquor in the sheet from washer to liquor in vat

$$R_v = W_p/W_v = [(1-C_{yp})/C_{yp}] / [(1-C_{yv})/C_{yv}]$$

Step-3 Calculation of ratio of liquor in the sheet from washer to liquor in shower

$$R_s = W_p/W_{ts} = W_p/(W_p + D)$$

Step-4 Calculation of ratio of liquor in sheet from washer to liquor to evaporators

$$R_e = W_p/W_e = W_p/(W_b + D)$$

Step-5 Calculation of ratio of shower liquor in the sheet from washer to total shower liquor

$$R_{gi} = R_s (S_v - S) / (S_v - S_s) = W_s/W_{ts} = R_s(DR_i) \quad , i=1, \dots, n$$

Step-6 Calculation of solid reduction ratio using formulas (1), (2), and (3)

$$(1) R_m = (1 - R_{gm} / R_s) [R_v + (1 - R_v) R_s] / (1 + R_s(1 - R_{gm} / R_s) (1 - R_v))$$

$$(2) R_a = (1 - R_{ga} / R_s) [R_v + (1 - R_v) R_s] / ((1 + R_s(1 - R_{ga} / R_s) (1 - R_v)) (\prod_{a+1 \rightarrow m} R_{a+1 \rightarrow m}) - R_{ga} (1 - \prod_{a+1 \rightarrow m} R_{a+1 \rightarrow m}))$$

$$(3) R_1 = (1 - R_{g1} / R_s) [R_v R_b + (1 - R_b R_v) R_e R_b] / ((1 + R_e(1 - R_{g1} / R_s) (1 - R_b R_v)) (\prod_{1 \rightarrow m} R_{1 \rightarrow m}) - R_{g1} (1 - \prod_{1 \rightarrow m} R_{1 \rightarrow m}))$$

Step-7 Calculation of solids in liquor from stock leaving stage final stage, %

$$S_m = R_1 * R_2 * \dots * R_m * S_b$$

Step-8 Calculation of total solids out with sheet, kg/tonne pulp

$$TS = S_m * W_p * FPR$$

Step-9 Calculation of total soda loss as Na₂SO₄, kg/tonne pulp

$$TSL = TS / 1.74$$

Step-10 Calculation of entrainment ratio

$$E = W_p(1 - DR)$$

Step-10 Calculation of percentage solid to evaporator

$$S_c = (W_b S_b - W_p S_m) / (W_b + D)$$

Step-11 Calculation of solids percentage in liquor from stock leaving stage

$$i, \quad \text{where } i=1, \dots, n$$

$$S_1 = R_1 * S_b \quad S_i = R_i * S_{i-1}$$

APPENDIX-II

Values of Gudmundson's Model Constants

CONSTANTS	VALUES	CONSTANTS	VALUES
1. P ₁	0.981	17. P ₁₇	21800
2. P ₂	1.000	18. P ₁₈	0.400
3. P ₃	0.2334	19. P ₁₉	19500
4. P ₄	-0.1006 X 10 ⁻⁰⁴	20. P ₂₀	2000
5. P ₅	0.1362 X 10 ⁻⁰⁹	21. P ₂₁	-95
6. P ₆	1.000	22. P ₂₂	15.00
7. P ₇	-0.07858	23. P ₂₃	0.120
8. P ₈	0.002735	24. P ₂₄	-0.001
9. P ₉	-0.01092 X 10 ⁻⁰⁴	25. P ₂₅	3.00
10. P ₁₀	-1.0200	26. P ₂₆	-0.025
11. P ₁₁	0.0476	27. P ₂₇	-0.120
12. P ₁₂	-0.3640 X 10 ⁻⁰³	28. P ₂₈	4300
13. P ₁₃	0.946 X 10 ⁻⁰⁶	29. P ₂₉	100
14. P ₁₄	-0.0515	30. P ₃₀	-14.0
15. P ₁₅	0.0505	31. P ₃₁	0.04
16. P ₁₆	0.0100		

APPENDIX-III

MULTIVARIATE LINEAR AND NONLINEAR REGRESSION ANALYSIS FOR DEVELOPMENT OF STATISTICAL EQUATIONS FOR WASHING, BLEACHING ENVIRONMENTAL PARAMETERS, MULTIPLE EFFECT EVAPORATOR, AND HIGH HEATING VALUE OF BLACK LIQUOR SOLIDS

Line of regression is the line which gives the best estimate of dependent variable for any given value of the independent variables. The term best fit in statistical sense is interpreted in accordance with the Principle of Least Squares which consists in minimizing the sum of the squares of the residuals or the errors of estimate i.e. the deviation between the given observed values of the variable and their corresponding estimate values as given by the line of best fit.

This is similar in principle to the way the mean of a group of data minimizes the scatter of the data when measured as the sum of the squares of deviation.

In this present investigation different kind of regression equations is to be used: Single variable linear or nonlinear and Multivariate linear or nonlinear equation.

One can write the most general type of linear model in variables X_1, X_2, \dots, X_k in the form

$$Y = \beta_0 Z_0 + \beta_1 Z_1 + \beta_2 Z_2 + \dots + \beta_p Z_p \quad (1)$$

$Z_0 = 1$ is a dummy variable which is always unity and will in general not be shown. However, it is sometimes mathematically convenient to have a Z_0 in the model.

Polynomial Models of Various orders in the X_j

First-Order models

1. If $p=1$ and $Z_1=X$ in Eq.(1), we obtain the simple first-order model with one predictor variable:

$$Y = \beta_0 + \beta_1 X_1 \quad (2)$$

2. If $p=k$ and $Z_j=X_j$, we obtain a first-order model with k predictor variables:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \dots + \beta_k X_k \quad (3)$$

Second-Order models

1. If $p=2$, $Z_1=X$, $Z_2=X^2$ and $\beta_2=\beta_{11}$, we obtain a second-order model with one predictor variables:

$$Y = \beta_0 + \beta_1 X_1 + \beta_{11} X_1^2 \quad (4)$$

2. If $p=5$, $Z_1=X_1$, $Z_2=X_2$, $Z_3=X_1^2$, $Z_4=X_2^2$, $Z_5=X_1 X_2$, $\beta_3=\beta_{11}$, $\beta_4=\beta_{22}$, and $\beta_5=\beta_{12}$ we obtain a second-order model with two predictor variables:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 \quad (5)$$

Models of any desired order can be represented by Eq.(1) by continuing the process illustrated above.

A general procedure for multiple regression are as follows

1. Transform raw data to any scale by normalizing all linear variable

2. Determine sample correlation coefficient
3. Find out the condition for the minimum of the function from the condition of the coefficient of the estimated regression coefficient
4. Define the system of normal equation which is usually for high order and can be solved by the computer
5. Find the coefficient of multiple correlation which may require correction for small size
6. For fewer degrees of freedom deduce corrected coefficient for multiple regression
7. Change back to natural scale
8. Find the error mean square(the replication variance)
9. Analyze the equation of regression statistically

The above analysis is readily adaptable to computer solution.

Therefore it is easier to solve through computer provided this analysis is done through matrix form.

$$\text{Pred. } y = b_0x_0 + b_1x_1 + b_2x_2 + \dots + b_kx_k$$

Where x_0 is a dummy variable equal to unity.

Now the raw statistical material is presented in matrix form. The matrix

$$X = \begin{bmatrix} x_{01} & x_{11} & \dots & x_{k1} \\ x_{02} & x_{12} & \dots & x_{k2} \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ x_{0n} & x_{1n} & \dots & x_{kn} \end{bmatrix}$$

will be called a matrix of independent variables, and the column vector

$$Y = \begin{bmatrix} y_1 \\ y_2 \\ \cdot \\ \cdot \\ \cdot \\ y_n \end{bmatrix}$$

will be called the observation vector. We also introduce a coefficient column of the form

$$B = \begin{bmatrix} b_0 \\ b_1 \\ \cdot \\ \cdot \\ b_k \end{bmatrix}$$

and the transpose of matrix X

$$X^T = \begin{bmatrix} x_{01} & x_{02} & \dots & x_{0n} \\ x_{11} & x_{12} & \dots & x_{1n} \\ \dots & \dots & \dots & \dots \\ x_{k1} & x_{k2} & \dots & x_{kn} \end{bmatrix}$$

The set of normal equations for estimating b_0, b_1, \dots, b_k has the form

$$b_0 \sum_{i=1}^n x_{0i}^2 + b_1 \sum_{i=1}^n x_{0i}x_{1i} + \dots + b_k \sum_{i=1}^n x_{0i}x_{ki} = \sum_{i=1}^n x_{0i}y_i$$

$$b_0 \sum_{i=1}^n x_{1i}x_{0i} + b_1 \sum_{i=1}^n x_{1i}^2 + \dots + b_k \sum_{i=1}^n x_{1i}x_{ki} = \sum_{i=1}^n x_{1i}y_i$$

.....

$$b_0 \sum_{i=1}^n x_{ki}x_{0i} + b_1 \sum_{i=1}^n x_{ki}x_{1i} + \dots + b_k \sum_{i=1}^n x_{ki}^2 = \sum_{i=1}^n x_{ki}y_i$$

in matrix form, they reduce to

$$X^T X B = X^T Y$$

Because multiplying matrix X^T by matrix X gives

$$X^T X = \begin{bmatrix} \sum x_{0i}^2 & \sum x_{0i}x_{1i} & \dots & \sum x_{0i}x_{ki} \\ \sum x_{1i}x_{0i} & \sum x_{1i}^2 & \dots & \sum x_{1i}x_{ki} \\ \dots & \dots & \dots & \dots \\ \sum x_{ki}x_{0i} & \sum x_{ki}x_{1i} & \dots & \sum x_{ki}^2 \end{bmatrix}$$

where $X^T X$ is the moment matrix. Multiplying matrix $X^T X$ by the B column vector gives a column vector

$$X^T X B = \begin{bmatrix} b_0 \sum x_{0i}^2 + b_1 \sum x_{0i}x_{1i} + \dots + b_k \sum x_{0i}x_{ki} \\ b_0 \sum x_{1i}x_{0i} + b_1 \sum x_{1i}^2 + \dots + b_k \sum x_{1i}x_{ki} \\ \dots \\ b_0 \sum x_{ki}x_{0i} + b_1 \sum x_{ki}x_{1i} + \dots + b_k \sum x_{ki}^2 \end{bmatrix}$$

Multiplying matrix X^T by the observation vector, Y , we obtain

$$X^T Y = \begin{bmatrix} \sum_{i=1}^n x_{0i} y_i \\ \sum_{i=1}^n x_{1i} y_i \\ \vdots \\ \sum_{i=1}^n x_{ki} y_i \end{bmatrix}$$

from eq.(6), the column vector B of coefficients is defined as

$$B = (X^T X)^{-1} X^T Y \tag{7}$$

Where $(X^T X)^{-1}$ is an inverse of matrix $(X^T X)$:

$$(X^T X)^{-1} = \begin{bmatrix} c_{00} & c_{01} & \dots & c_{0k} \\ c_{10} & c_{11} & \dots & c_{1k} \\ \vdots & \vdots & \ddots & \vdots \\ c_{k0} & c_{k1} & \dots & c_{kk} \end{bmatrix} \tag{8}$$

The elements of the inverse matrix are defined by the relation

$$c_{ju} = (1/\Delta) (\sum_{i=1}^n x_{ui} x_{ji}) \tag{9}$$

Where Δ is the determinant of product matrix $X^T X$, $(\sum_{i=1}^n x_{ui} x_{ji})$ is the cofactor of the element $(\sum_{i=1}^n x_{ui} x_{ji})$ in matrix $X^T X$.

For an inverse matrix to exist, matrix $X^T X$ must be nonsingular. Therefore, in using this method of calculation, it is important that the variables x_1, x_2, \dots, x_k be linearly independent variables will not be a linear combination of the respective elements in other columns.

To find the residual mean square, one should evaluate the pred. Y column vector

$$\text{Pred. } Y = \begin{bmatrix} \text{Pred. } y_1 \\ \text{Pred. } y_2 \\ \vdots \\ \text{Pred. } y_n \end{bmatrix} = XB$$

The numerator of the residual mean square is found by multiplying the matrices together:

$$[Y - \text{pred. } Y]^T [Y - \text{pred. } Y] = \sum_{i=1}^n (y_i - \text{pred. } y_i)^2 \tag{10}$$

let β designate the column vector of true regression coefficients and let the expected value of B $E(B)=\beta$. Then

$$E\{[B-\beta][B-\beta]^T\} = \begin{bmatrix} \sigma_{b0}^2 & C_{0b0b1} & \dots & C_{0b0bk} \\ C_{0b0b1} & \sigma_{b1}^2 & \dots & C_{0b1bk} \\ \dots & \dots & \dots & \dots \\ C_{0bkb0} & C_{0bkb1} & \dots & \sigma_{bk}^2 \end{bmatrix} \quad (1)$$

Where $\sigma_{b_j}^2$ is the variance of b_j , $Cov_{b_jb_k}$ is the covariance, or the correlation moment between b_j and b_k . Thus, the diagonal terms of the matrix are the coefficient variances required for significance testing, while the non diagonal terms are the covariances of the respective regression estimators determining the statistical relationship between the coefficients.

Let the matrix $E\{[B-\beta][B-\beta]^T\} = E\{(X^T X)^{-1} X^T Y^0 [(X^T X)^{-1} X^T Y^0]^T\}$

Where Y^0 is a random normal vector with independent elements having a variance of σ_y^2 :

$$Y^0 = Y - E(Y) = \begin{bmatrix} y_1 - m(y_1) \\ y_2 - m(y_2) \\ \vdots \\ y_n - m(y_n) \end{bmatrix}$$

The coefficient matrix of normal equations is symmetrical, and so

$$[(X^T X)^{-1}]^T = (X^T X)^{-1}$$

Putting $\sigma_{y1}^2 = \sigma_{y2}^2 = \dots = \sigma_{yn}^2 = \sigma_y^2$ and recalling that errors are statistically independent, we get

$$E\{Y^0 Y^{0T}\} = \begin{bmatrix} \sigma_{y1}^2 & & & 0 \\ & \sigma_{y2}^2 & & \\ & & \dots & \\ 0 & & & \sigma_{yn}^2 \end{bmatrix} = C \sigma_y^2 \quad (12)$$

Thus, we have

$$E\{(B-\beta)(B-\beta)^T\} = (X^T X)^{-1} \sigma_y^2 \quad (13)$$

whence

$$\sigma_{b_j}^2 = c_{jj} \sigma_y^2, \quad Cov_{b_jb_u} = c_{ju} \sigma_y^2 \quad (14)$$

The matrix $(X^T X)^{-1}$ is called an error matrix, or a variance-(covariance) matrix.

Since the variance matrix is non-diagonal and, as a consequence, all regression coefficients are interrelated, each coefficient cannot be tested for significance separately. Therefore, the relation

$$t_j = |b_j| / s_y \sqrt{c_{jj}} \quad (15)$$

can only be looked upon as a means for ranking the factors. A procedure has been proposed for consecutively eliminating insignificant factors: a factor for which t_j is the least is dropped and the calculation is repeated, as long as the residual mean square decreases. This improves the interpolating properties of the regression equation, but the resultant coefficients are biased estimates. With a larger number of factors, the calculation of multiple regression calls for the use of a digital computer.

The Method of Least Squares:

$F(x)$ be a class of functions which impose an equal number l of constraints on the sample. The number of constraints l is equal to the number of indefinite coefficients entering the analytic expression for this function. Most frequently, resort is made to polynomials of various powers. The best approximate regression equation is yielded by that function out of the class in question for which the sum of squares

$$\phi = \sum [y_i - f(x_i)]^2 \quad (1)$$

yields the lowest value.

When the random variables involved are normally distributed, the method of least squares is treated in probability theory as a special case of the maximum likelihood principal. In the circumstances, we may invoke sufficient statistics, that is, functions of observations (estimates of population parameters) with the aid of which we can extract all information about the population parameters from the observations.

The problem of determining the regression equation parameters practically reduces to finding the maximum of a function of many variables. the function

$$\text{Pred. } y = f(x, b_0, b_1, b_2, \dots) \quad (2)$$

is differentiable and we are to choose b_0, b_1, b_2, \dots such that

$$\phi = \sum [y_i - f(x_i, b_0, b_1, b_2, \dots)]^2 = \min \quad (3)$$

a necessary condition for $\phi(b_0, b_1, b_2, \dots)$ to be a minimum is to satisfy the following equalities

$$\partial\phi/\partial b_0 = 0, \partial\phi/\partial b_1 = 0, \dots \quad (4)$$

or

$$\begin{aligned} \sum [y_i - f(x_i, b_0, b_1, b_2, \dots)] \partial f(x_i) / \partial b_0 &= 0 \\ \sum [y_i - f(x_i, b_0, b_1, b_2, \dots)] \partial f(x_i) / \partial b_1 &= 0 \end{aligned} \quad (5)$$

on rearranging,

$$\begin{aligned} \sum y_i (\partial f(x_i) / \partial b_0) - \sum f(x_i, b_0, b_1, b_2, \dots) (\partial f(x_i) / \partial b_0) &= 0 \\ \sum y_i (\partial f(x_i) / \partial b_1) - \sum f(x_i, b_0, b_1, b_2, \dots) (\partial f(x_i) / \partial b_1) &= 0 \end{aligned} \quad (a1)$$

equations(a1) are as many as there are unknown coefficients b_0, b_1, b_2, \dots in the regression equation in mathematical statistics, they are known as a set of normal equations.

At any values of b_0, b_1, b_2, \dots , the quantity ϕ is greater than or equal to zero, so it must have at least one minimum. Therefore, if the set of normal equations has a unique solution, this solution is the minimum for ϕ . Equations(a1) cannot be solved in the general form. For their solution, we must specify a particular form for the function f .

APPENDIX-IV

LINEAR PROGRAMMING WITH CONSTRAINTS(SIMPLEX METHOD) TO OPTIMIZE A MULTI-STAGE BLEACH PLANT

The Simplex Algorithm:

For the solution of any L.P.P. by simplex algorithm , the existence of an initial basic feasible solution is always assumed. The steps for the computation of an optimum solution are as follows:

Step 1. Check whether the objective function of the given L.P.P. is to be maximized or minimized.If it is to be minimized then we convert it into a problem of maximizing it by using the result. Minimum $z = -\text{Maximum}(-z)$.

Step 2. Check whether all $b_i(i=1,2,\dots,m)$ are non negative.If any one of b_i is negative then multiply the corresponding equation of the constrains by -1 , so as to get all $b_i(I=1,2,\dots,m)$ non negative.

Step 3. Convert all the inequations of the constrains into equations by introducing slack and/ or surplus variables in the constrains . Put the costs of these variables equal to zero.

Step 4. Obtain an initial basic feasible solution to the problem in the form $x_b = B^{-1}b$ and put it in the first column of the simplex table.

Step 5. Compute the net evaluations $z_j - c_j$ ($j=1,2,3,\dots,n$) by using the relation $z_j - c_j = C_b y_j - c_j$.

Examine the sign $z_j - c_j$.

1. if all $(z_j - c_j) > 0$ then the initial basic feasible solution x_b is an optimum basic feasible solution.
2. If at least one $(z_j - c_j) < 0$, proceed on to the next step.

Step 6. If there are more than one negative $z_j - c_j$, the most negative of them. Let it be $z_r - c_r$ for some $j=r$.

1. if all $y_{ir} < 0$ ($i=1,2,\dots,m$), then there is an unbounded solution to the given problem.
2. If at least one $y_{ir} > 0$ ($i=1,2,\dots,m$) then the corresponding vector y_r enters the basis y_b .

Step 7. Compute the ratios $\{x_{bk}/y_{kr}, y_{ir} > 0, I=1,2,\dots,m\}$ and choose the minimum of them . Let the minimum of these ratios be x_{bk}/y_{kr} . Then the vector y_k will level the basis y_b . The common element y_{kr} , which is in the k^{th} row and the r^{th} column as the leading element (or pivotal element) of the table.

Step 8. Convert the leading element to unity by dividing its row by the leading element itself and all other elements in its column to zeroes by making use of the relations:

$$y_{ij} = y_{ij} - y_{kj}/y_{kr} y_{ir} \quad i=1,2,3,\dots,m+1; i \neq k$$

$$y_{kj} = y_{kj} / y_{kr}$$

$$j=0,1,2,\dots,n$$

Step 9. Go to step 5 and repeat the computational procedure until either an optimum solution is obtained or there is an indication of an unbounded solution

APPENDIX-V

NONLINEAR PROGRAMMING WITH CONSTRAINTS TO OPTIMIZE MULTISTAGE BROWN STOCK WASHING PROBLEM:

Optimization (maximization or minimization) of an objective function with constraints is done by using the software Mathcad 8. The general form for using system solving functions in Mathcad is within the body of a solve block. There are four general steps to creating a solve block. These are:

1. Provide an initial guess for each of the unknowns you intent to solve for. Mathcad solves equations by making iterative calculations that ultimately converge on the right answer. The initial guesses one provide give Mathcad a place to start searching for solutions.
2. Type the word *Given* in a separate math region below the guess definitions. This tells Mathcad that what follows is a system of constraints equations.
3. Now enter the constraint equations(equalities and inequalities)in any order below the word *Given*.
4. Enter any equation that involves one of the functions Find, Maximize, Minimize, or Minerr below the constraints.

Tolerances for solving

Mathcad's numerical solvers make use of tolerance parameter in calculating solutions in solve block.

Constraint tolerance:

This parameter, determined by the value of the built-in variable CTOL, controls how closely a constraint must be met for a solution to be acceptable. For example, if the constraint tolerance were 0.0001, a constraint such as $x < 2$ would be considered satisfied if, in fact, the values of x satisfied $x < 2.0001$.

Non-Linear Programming Problem:

z be a real valued function of n variables defined by

(a) $z = f(x_1, x_2, \dots, x_n)$

$\{b_1, b_2, \dots, b_m\}$ be a set of constants such that

(b)
$$\left\{ \begin{array}{l} g^1(x_1, x_2, \dots, x_n) \{<=, >= \text{ or } =\} b_1 \\ g^2(x_1, x_2, \dots, x_n) \{<=, >= \text{ or } =\} b_2 \\ \cdot \\ g^m(x_1, x_2, \dots, x_n) \{<=, >= \text{ or } =\} b_m \end{array} \right.$$

where g 's are real valued functions of n variables, x_1, \dots, x_n . finally,

$$(c) \quad x_j \geq 0, \quad j=1,2,\dots,n$$

either $f(x_1, \dots, x_n)$ or some $g^i(x_1, \dots, x_n)$, $i=1,2,\dots,m$; or both are nonlinear, the problem of determining the n -type (x_1, x_2, \dots, x_n) which makes z a maximum or minimum satisfies (b) and (c), is called a general non linear programming problem.

• **Fletcher and Reeves Algorithm:**

The algorithm given by Fletcher and Reeves is summarized as follows:

1. Start with an arbitrary initial point X_1 .
2. Set the first search direction $S_1 = -\nabla f(X_1) = -\nabla f_1$
3. Find the point X_2 according to the relation

$$X_2 = X_1 + \lambda_1^* S_1$$

Where λ_1^* is the optimal step length in the direction S_1 . Set $I=2$ and go to the next step.

4. Find $\nabla f_i = \nabla f(X_i)$, and set
5. $S_i = -\nabla f_i + (|\nabla f_i|^2 / |\nabla f_{i-1}|^2) S_{i-1}$
6. Compute the optimum step length λ_i^* in the direction S_i , and find the new point

$$X_{i+1} = X_i + \lambda_i^* S_i$$

Test for the optimality of the point X_{i+1} . If X_{i+1} is optimum, stop the process. Otherwise, set the value of $i=i+1$, and repeat step(4),(5) and (6)

APPENDIX-VI

Results of Chap-2

Following results are obtained for various DF and N. These are depicted in Table-1 .

Table-1 Effect of DF and N on % solids to evaporator, soda loss, total soda loss

DF	% solids to evaporator			Soda loss			Total solid loss		
	N=2	N=3	N=4	N=2	N=3	N=4	N=2	N=3	N=4
0.0	23.67	24.41	24.69	134.11	100.89	88.20	233.35	175.54	153.47
0.5	22.81	23.53	23.86	107.49	72.66	57.17	187.04	126.42	99.48
1.0	22.00	22.64	22.94	82.77	50.494	35.20	144.02	87.85	61.26
1.5	21.16	21.71	21.96	64.76	35.35	21.55	112.68	61.51	37.50
2.0	20.31	20.78	20.99	52.18	23.35	13.42	90.79	44.11	23.35
2.5	19.53	19.91	20.07	40.24	17.43	8.08	70.03	30.33	14.06
3.0	18.78	19.08	19.19	30.47	11.96	4.89	53.03	20.81	8.51
3.5	18.05	18.29	18.37	24.17	8.60	3.11	42.05	14.97	5.42
4.0	17.36	17.55	17.61	19.39	6.28	2.04	33.75	10.93	3.56
4.5	16.73	16.87	16.91	14.18	4.10	1.19	24.67	7.45	2.07
5.0	16.09	16.22	16.26	12.84	3.47	.94	22.35	6.04	1.63

Table-2 Power Consumption and liquor to spray per tonne of pulp, Steam consumption for hot wash water in washing operation as a function of dilution factor

DF	Liquor to evaporator, kg/t pulp	Liquor to spray, kg/t	P_2 , kW/t Eq.(2.15)	steam consumption, kg/t Eq.(2.38)
0	8348	79508.0	0.2429	303.67
0.5	8769	79929.5	0.2442	332.59
1.0	9213	80373.5	0.2456	361.52
1.5	9671	80831.5	0.2468	390.45
2.0	10138	81298.5	0.2484	419.36
2.5	10612	81772.5	0.2498	448.28
3.0	11091	82251.0	0.2513	477.19
3.5	11573	82733.0	0.2528	506.12
4.0	12058	83218.0	0.2543	535.04
4.5	12544	83704.5	0.2557	563.96
5.0	13031	84191.5	0.2572	592.88

APPENDIX-VII

Results of Chap-3

Table-1 Effect of dilution factor on steam consumption for MEE.

DF	Steam Consumption, kg/s		
	N=2	N=3	N=4
0	2.3507	2.3168	2.3084
0.5	2.3850	2.3550	2.3422
1.0	2.4196	2.3936	2.3807
1.5	2.4589	2.4327	2.4240
2.0	2.4942	2.4765	2.4677
2.5	2.5299	2.512	2.5076
3.0	2.5660	2.5524	2.5479
3.5	2.5978	2.5887	2.5841
4.0	2.6298	2.6206	2.6161
4.5	2.6575	2.6529	2.6483
5.0	2.902	2.6809	2.6763

APPENDIX-VIII

Table-1 Coefficients of equation 4.9, 4.11 and 4.13

i	a _i		b _i		c _i	
	Ref.(23)	Present	Ref.(23)	Present	Ref(23)	Present
0	33.5	7.67	80.0	1.977	7.0	1.633
1	0.5	.072	-25.0	-1.118	0.2	0.276
2	-0.15	-0.068	2.5	11.86	0.3	9.797
3	-0.1	-0.014	0.3	0.054	0.3	0.038
4	-0.03	-0.011	0.01	0.019	0.01	.003296

Table- 2 Results(optimum conditions) for final stage brightness 90.88 GE

Stage	Chemical Addition kg/tonne		Temperature, °C		Brightness or Kappa number	
	Ref.(23)	Present	Ref.(23)	Present	Ref.(23)	Present
C E	71.42	60*	37.77	40	4.46	4.46
D	2.23	6	60	60	75.0	74.81
E D	15.63	6.69**	80.55	70	88.0	90.88

Note: * C=53.52 kg/t and E=6.48 kg/t; **E= 3.89 kg/t and D=2.80 kg/t

Table- 3 Results(optimum conditions,change in temperature and chemical used) for final stage brightness 89.228 GE

Stage	Chemical Addition kg/tonne		Temperature, °C		Brightness or Kappa number	
	Ref.(23)	Present	Ref.(23)	Present	Ref.(23)	Present
C E	71.42	53	37.77	45	4.46	4.46
D	2.23	6.1	60	65	75.0	76.266
E D	15.63	6.5	80.55	65	88.0	89.228

Decrease in chemical used in (CE),(ED) stage and slightly increase in chemical used in D stage and decrease in (ED) stage temperature and increase in (CE) and D stage shows the impact of temperature and chemical used on final stage brightness.

Table- 4 Results(optimum conditions, change in temperature) for final stage brightness 90.35 GE

Stage	Chemical Addition kg/tonne		Temperature, °C		Brightness or Kappa number	
	Ref.(23)	Present	Ref.(23)	Present	Ref.(23)	Present
C E	71.42	60	37.77	43	4.46	4.46
D	2.23	6	60	55	75.0	74.54
E D	15.63	6.69	80.55	58	88.0	90.35

Decrease in (ED) and Dstage temperature and increase in (CE) stage shows the impact of temperature on final stage brightness.

Table- 5 Results(optimum conditions, change in chemical used) for final stage brightness 93.919 GE

Stage	Chemical Addition kg/tonne		Temperature, °C		Brightness or Kappa number	
	Ref.(23)	Present	Ref.(23)	Present	Ref.(23)	Present
C E	71.42	56	37.77	40	4.46	4.46
D	2.23	6.6	60	60	75.0	81.93
E D	15.63	6.8	80.55	70	88.0	93.919

Decrease in chemical used in (CE) stage and slightly increase in chemical used in D, (ED) stag shows the impact of chemical used on final stage brightness.

Table-6 Equations for estimating AOX

AOX=k₁[ACl₂+k₂AcIO⁻+k₃AcIO₂+ k₄ClO₂] +k₅							
S.No.	k ₁	K ₂	k ₃	k ₄	k ₅	References	Remark
1.	0.089	0.0	0.0526	0.301	0.0	(105)	Softwood with O ₂ delignification
2.	0.1	0.0	0.2	0.0	0.0	(8)	Oxygen predelignified softwood pu (kappa number 18) bleaching sequenc (C+D) or (DC)ED(EP)D
3.	0.086	0.0	0.279	0.0	0.0	(62)	Oxygen delignified (softwood)pu kappa number17.7bleachingsequenc (C50+D50)(EO)D
4.	0.1	0.6	0.2	0.0	0.0	(83)	ECF bleaching Sequence of C delignified hardwood & bagasse pulps
AOX=k₁(AIT)+k₂(AIT)²+k₃(AIT*kappa)+k₄ Where AIT=(%Cl ₂ +0.526%ClO ₂)							
5.	1.04	-0.156	0.0132	0.0	0.0	(115)	in the first two bleaching stages : atomic chlorine application rates of less than 3%
6.	0.0	0.0	0.032	0.028	0.0	(115)	southern pine pulp kappa31,13 and 1 (DC)E _{Op} sequence R ² =0.93
AOX=k₁(%D)+k₂(CF)+k₃(%D)²+k₄(CF*%D)+k₅ Where %D=%ClO ₂ , CF=charge factor							
7.	9.85E-03	2.0857	-8.5E-05	-0.01676	-0.21597	(8)	As above R ² =0.963
AOX=k₁(X₁)+k₂(X₂)^a+k₃(X₃)²+k₄(X₄)^b+k₅ X ₁ =washing,X ₂ =initial kappa no.,X ₃ =pH, X ₄ =kappa factor							
8.	0.5802	-1	0.052	1	1.10	(73)	a=-0.299, b=0.9893,c= D(L) & D(G) delignification of softwood kraft and extended kraf pulps(kappa no.35-12 bleaching sequence D(gas)EDED(kappa no.30-35) R ² =0.88
9.	0.0	0.011	0.0	1	0.053	(73)	a=1, b=0.2303 R ² =0.92
10.	0.0	0.006	0.0	0.852	0.0527	(73)	a=1, b=0.2303 R ² =0.92
AOX=k₁e^(k₂+k₃DE)+k₄ Where DE=DE kappa no.							
11.	1.0	2.18	-0.51	0.95	0.0	(11)	For washing between D0 &E stages R ² =0.88
12.	0.45	1.8	-0.49	0.48	0.0	(11)	For no washing between D0 &E stages R ² =0.83

Table-7 Comparison of Computed AOX values with Experimental data due to various investigators

Equation	1	2	3	4	5	6	7	8	9	10	Pr
AOX (est.) ka, 12.9	1.40	1.39	1.20	1.39	1.65	.758	1.65	1.35	.769	.61	1.
AOX _{measured} =1.50											
Absolute error	0.10	0.11	0.30	0.11	-0.15	.742	-0.15	-0.15	0.731	0.89	-0
%error	6.89	7.2	19.73	7.2	-10.0	49.46	-10.0	-10.0	48.73	59.33	-9
AOX (est.) ka, 18.3	2.59	2.77	2.27	2.77	2.44	1.77	2.78	1.45	0.89	0.71	2.
AOX _{measured} =2.70											
Absolute error	0.11	-0.07	0.43	-0.07	0.26	0.92	-0.08	1.25	1.81	1.99	-
%error	3.99	-2.66	15.91	-2.66	9.76	34.17	-2.89	46.29	66.87	73.78	-
AOX (est.) ka, 22.3	3.30	3.53	2.87	3.53	2.81	2.69	2.97	1.49	1.40	1.126	2
AOX _{measured} =2.90											
Absolute error	-0.40	-0.63	0.028	-0.63	0.09	0.22	-0.07	1.41	1.49	1.77	-0
%error	-13.84	-21.27	0.96	-21.27	3.24	7.35	-2.27	48.62	51.6	61.16	-1
AOX (est.) ka, 32.9	4.84	5.20	4.24	5.20	3.40	5.82	2.96	2.90	1.52	1.19	2.
AOX _{measured} =4.20											
Absolute error	-0.64	-1.0	-0.04	-1.0	0.80	-1.60	1.23	1.29	2.68	3.0	1
%error	-15.16	-24	-0.89	-24	19.28	38.48	29.49	30.87	63.86	71.67	2

Note: % Error = (measured data-estimated data)/measured

Table-8 Comparison of AOX values from regression equation

Equation	5	6	7	8	9	10	Present
AOX (est.) ka, 12.9	1.65	.758	1.65	1.35	.769	.61	1.64
AOXmeasured=1.50							
Absolute error	-0.15	.742	-0.15	-0.15	0.731	0.89	-0.14*
%error	-10.0	49.46	-10.0	-10.0	48.73	59.33	-9.33
AOX (est.) ka, 18.3	2.44	1.77	2.78	1.45	0.89	0.71	2.76
AOXmeasured=2.70							
Absolute error	0.26	0.92	-.08	1.25	1.81	1.99	-.06
%error	9.76	34.17	-2.89	46.29	66.87	73.78	-2.22*
AOX (est.) ka, 22.3	2.81	2.69	2.97	1.49	1.40	1.126	2.95
AOXmeasured=2.90							
Absolute error	0.09	0.22	-0.07	1.41	1.49	1.77	-0.05
%error	3.24	7.35	-2.27	48.62	51.6	61.16	-1.74*

Table-9 Comparison of COD values

Equation	1	Present
COD est., kappa no. 31, KF=0.05	56.24	54.62
COD measured=43.88		
Absolute error	-12.36	-10.74
% error	-28.16	-24.47*
COD est., kappa no. 13, KF=0.05	18.63	15.79
COD measured=15.35		
Absolute error	-3.28	-3.27
% error	-21.36	-21.30*
COD est., kappa no. 14, KF=0.05	20.71	23.80
COD measured=23.03		
Absolute error	2.32	-0.77
% error	10.07	-3.34*

Table- 10 Comparison of Color values

Equation	3	4	Present(1)	Present(2)
Color est. kappa no. 31, KF=0.15, COD=62.16	101.76	96.87	108.91	94.29
Color measured=95.08				
Absolute error	-6.68	-1.79	-13.83	0.78
% error	-7.02	-1.85	-14.54	0.82
Color est. kappa no. 13, KF=0.15, COD=24.13	41.51	38.38	50.85	39.54
Color measured=51.19				
Absolute error	9.68	12.80	0.33	11.64
% error	18.90	25.02	0.65	22.75
Color est., kappa no. 14, KF=0.15, COD=32.18	44.85	50.76	41.63	44.62
Color measured=40.22				
Absolute error	-4.64	-10.54	-1.42	-4.39
% error	-11.53	-26.21	-3.53	-10.91

APPENDIX-IX

Table-1 Components in Black Liquors and Percentage of dry solids

Wood	Pine	Pine	Pine	Pine	Pine	Spruce
Dry solids in sample, %	17	58	37.5	54.3	14	
Lignin	28.9	30.7	31.1	42	43	41
Hemicellulose & sugars	1.14	0.11	1.3			
Extractives	6.69	2.53	5.7			3
Saccharinic acids				18.8	27	28
Acetic acid	3.52	2.08	5.2	3.83	9	5
Formic acid	4.48	2.70	3.1	3.37		3
Other organic acids	5.5	2.22				
Methanol						1
Unknown organic compounds	19.0	29.5	5.8			
Inorganic salts	18.6	18.5	20.3	25.6	14	
Organically combined Na	10.1	10.3	8.7			
Unknown inorganic compounds	2.08	1.35				
Sulphur, S						3
Sodium, Na						16
Total	100	100	100			100

Table-2 Computed data of steam production, total heating value of black liquor solids, d organics and inorganics and black liquor solids as a function of dilution factor and nu of washers(basis 1 tonne of pulp).

No. of washers=2					
DF	BLS	HV(org)	HV(ino)	HV total	steam
0.0	1.97	2.860	160170	2.877	6559.39
0.5	2.00	2.904	162610	2.921	6659.89
1.0	2.02	2.933	164236	2.950	6725.81
1.5	2.046	2.988	166350	2.971	6812.47
2.0	2.059	2.990	167407	3.007	6855.81
2.5	2.069	3.005	168220	3.021	6887.16
3.0	2.082	3.023	169277	3.040	6930.49
3.5	2.088	3.032	169764	3.049	6951.23
4.0	2.093	3.039	170171	3.056	6966.91
4.5	2.098	3.047	170577	3.064	6985.81
5.0	2.103	3.054	170984	3.071	7001.48
No. of washers=3					
DF	BLS	HV(org)	HV(ino)	HV total	Steam
0.0	1.850	2.958	165618	2.975	6782.97
0.5	1.870	2.997	167813	3.014	6871.48
1.0	1.890	3.029	169594	3.046	6944.46
1.5	1.910	3.060	171342	3.077	7014.76
2.0	1.913	3.061	171366	3.078	7017.57
2.5	1.918	3.068	171789	3.085	7032.97
3.0	1.921	3.073	172054	3.090	7044.54
3.5	1.922	3.074	172098	3.091	7047.07
4.0	1.923	3.075	172155	3.092	7049.33
4.5	1.924	3.076	172163	3.093	7052.42
5.0	1.928	3.085	172700	3.010	7072.33
No. of washers 4					
DF	BLS	HV(org)	HV(ino)	HV total	Steam
0.0	1.870	2.993	167569	3.017	6885.30
0.5	1.899	3.038	170122	3.056	6967.73
1.0	1.919	3.069	171878	3.087	7037.21
1.5	1.929	3.085	172773	3.103	7073.21
2.0	1.932	3.090	173017	3.108	7086.30
2.5	1.933	3.092	173171	3.110	7090.13
3.0	1.936	3.097	173399	3.114	7099.16
3.5	1.937	3.098	173415	3.115	7102.11
4.0	1.938	3.099	173504	3.116	7103.82
4.5	1.959	3.132	175374	3.150	7181.73
5.0	1.964	3.141	175862	3.160	7205.69

HV(org)= 10^7 kJ/tonne pulp, HV(ino)=kJ/tonne pulp, HV total= 10^7 kJ/tonne pulp
Steam to mill,kg/tonne pulp

APPENDIX-X

COMPUTER PROGRAMS

```
/* PROGRAM FOR SOLID REDUCTION RATIO AND MATERIAL BALANCE OF FOUR STA
BSW*/
#include<fstream.h>
#include<conio.h>
void main()
{ // clrscr();
  float D;
  float Sb,Cb,Cv,Cs,Cbt,DR[4],Rg[4], Pulp;
  ifstream inn("INPUT4.TXT");
  //cout<<"\nEnter Blow Tank Soluble Solids(Sb)%:";
  inn>>Sb;
  //cout<<"\nEnter dilution factor(D):";
  inn>>D;
  //cout<<"\nEnter Consistency of Pulp from Blow Tank(Cb) (%/100):";
  inn>>Cb;
  //cout<<"\nEnter Vat Consistencies(Cv) (%/100):";
  inn>>Cv;
  //cout<<"\nEnter Sheet Consistencies(Cs) (%/100):";
  inn>>Cs;
  //cout<<"\nEnter Blow Pit Consistencies(Cbt) (%/100):";
  inn>>Cbt;
  //cout<<"\nEnter Pulp:";
  inn>>Pulp;
  for(int j=0;j<4;j++)
  { //cout<<"\nEnter displacement ratio:";
    inn>>DR[j];
  }
  ofstream out("OUTPUT4.TXT");
  float Wb=(1-Cb)/Cb;
  out<<"\n% weight of undiluted blow liquor(Wb):"<<Wb;
  float Wp=(1-Cs)/Cs;
  out<<"\n% weight of liquor in the sheet from washer(Wp):"<<Wp;
  float Wv=(1-Cv)/Cv;
  out<<"\n% weight of liquor in the vat(Wv):"<<Wv;
  float Wts=Wp+D;
  out<<"\n% weight of liquor in the shower(Wts):"<<Wts;
  float We=Wb+D;
  out<<"\n% weight of liquor to evaporators(We):"<<We;
  float Rb=Wb/Wp;
  out<<"\nratio of undiluted blow liquor to liquor in sheet from
washer(Rb):"<<Rb;
  float Rv=Wp/Wv;
  out<<"\nratio of liquor in the sheet from washer to liquor in
vat(Rv):"<<Rv;
  float Rs=Wp/Wts;
  out<<"\n ratio of liquor in the sheet from washer to liquor in
shower(Rs):"<<Rs;
  float Re=Wp/We;
```

```

out<<"\nratio of liquor in sheet from washer to liquor to
evaporators(Re):"<<Re;
for(int j=0;j<4;j++)
{
Rg[j]=Rs*DR[j];
out<<"\n Rg:"<<Rg[j];
}
float R4=((1-Rg[3]/Rs)*(Rv+(1-Rv)*Rs))/((1+Rs*(1-Rg[2]/Rs)*(1-Rv));
out<<"\nsolids reduction ratio of stage 4(R4):"<<R4;
float R3=((1-Rg[2]/Rs)*(Rv+(1-Rv)*Rs))/((1+Rs*(1-Rg[2]/Rs)*(1-Rv)*R4)-
(Rg[2]*(1-R4)));
out<<"\nsolids reduction ratio of stage 3(R3):"<<R3;
float R2=((1-Rg[1]/Rs)*(Rv+(1-Rv)*Rs))/((1+Rs*(1-Rg[1]/Rs)*(1-
Rv)*R4*R3)-(Rg[2]*(1-R3*R4)));
out<<"\nsolids reduction ratio of stage 2(R2):"<<R2;
float R1=((1-Rg[0]/Rs)*(Rb*Rv+(1-Rb*Rv)*Re*Rb))/((1+Re*(1-Rg[0]/Rs)*(1-
Rv*Rb)*R2*R3*R4)-(Rg[0]*(1-R2*R3*R4)));
out<<"\nsolids reduction ratio of stage 1(R1):"<<R1;
float Sm=R4*R3*R2*R1*Sb;
out<<"\nsolids in liquor from stock leaving stage M(final
stage)%(Sm):"<<Sm;
float Smb=((Wb*Sb)-(Wp*Sm))/(Wb+D);
out<<"\n solids to evaporator(Smb)%:"<<Smb;
float TSS=(Sm*Wp)/100;//kg/ton O.D.pulp(1000/100=10)
out<<"\ntotal solids out with sheet(kg/ton pulp):"<<TSS;
float S1=R1*Sb;
out<<"\nsolids in liquor from stock leaving stage 1,%(S1):"<<S1;
float S2=R2*S1;
out<<"\nsolids in liquor from stock leaving stage 2,%(S2):"<<S2;
float S3=R3*S2;
out<<"\nsolids in liquor from stock leaving stage 3,%(S3):"<<S3;
float S4=R4*S3;
out<<"\nsolids in liquor from stock leaving stage 4,%(S4):"<<S3;
float TCL=Pulp*TSS;
out<<"\ntotal chemical loss per cook(kg):"<<TCL;
float TSL=TCL/1.74;
out<<"\ntotal soda loss as Na2SO4(kg/ton pulp):"<<TSL;
// Material Balnce :
float WW=((Wp*Pulp)-TCL)+((D*Pulp));
out<<"\ntotal wash water required:"<<WW;
float lv=Wv*Pulp;
out<<"\n liquor in vat:"<<lv;
float lp=Wp*Pulp;
out<<"\n liquor with pulp:"<<lp;
float lb=lv-lp;
out<<"\n liquor Stream(b):"<<lb;
float lf=lb+WW;
out<<"\n liquor Stream(f):"<<lf;
float Wbt=(1-Cbt)/Cbt;
out<<"\n% Weight of liquor from blow Tank(Wbt):"<<Wbt;
float lbto=Wbt*Pulp;
out<<"\n liquor from blow Tank(lbto):"<<lbto;
float lbti=Wb*Pulp;

```

```

out<<"\n liquor to blow Tank(lbti):"<<lbti;
float le=lbto-lbti;
out<<"\n liquor stream E(le):"<<le;
float lev=lv-lbto;
out<<"\n liquor to Evaporator(lev):"<<lev;
// Solids from Digester:
float Sb1=(Sb*lbti);
out<<"\n Solids from Digester(Sb1):"<<Sb1;
// Solid Balance Across 4th Stage:
float St4=(lp*(S3-S4))/(lf-lb);
out<<"\n Solids Going to seal Tank 4:"<<St4;
// Solid Balance Across 3rd Stage:
float St3=((WW*St4)+(lp*(S2-S3)))/(lf-lb);
out<<"\n Solids Going to seal Tank 3:"<<St3;
// Solid Balance Across 2nd Stage:
float St2=((WW*St3)+(lp*(S1-S2)))/(lf-lb);
out<<"\n Solids Going to seal Tank 2:"<<St2;
// Solid Balance Across 1st Stage:
float St= lf-le-lev;
float St1=((WW*St2)+Sb1-(lp*S1))/St;
out<<"\n Solids Going to seal Tank 1:"<<St1;
//getch();
}

```

/* PROGRAM TO ESTIMATE OPTIMUM NUMBER OF EFFECTS OF MEE*/

```

#include<fstream.h>
//#include<conio.h>
#include<math.h>
float totcost[10];
void main()
{
float pl,a,pfc
,mvi,y,hvn,cpw,t2,t1,pcw,ps,m,w,vstd,pic,et,pastd,vastd,a1,a5,p1;
float f0,b,F,f,O,S,D,k1,R,D1,cpi,cpa,cpc,rcw,Cc ;
ifstream inn("opt.txt");
ofstream out("opdat.txt");
inn>>pl;inn>>a;inn>>pfc;inn>>mvi;inn>>y;inn>>hvn;inn>>cpw;inn>>t2;inn>>t
1;inn>>pcw;inn>>ps;inn>>m;inn>>w;inn>>vstd;inn>>pic;inn>>et;inn>>pastd;i
nn>>vastd;inn>>a1;inn>>a5;inn>>p1;
inn>>f0;inn>>b;inn>>F;inn>>f;inn>>O;inn>>S;inn>>D;inn>>k1;inn>>R;inn>>D1
;inn>>cpi;inn>>cpa;inn>>cpc;inn>>rcw;inn>>Cc;
for(int N=1,K=1;N<10,K<10;N++,K++)
{
float y1=pow(y,2/y);
out<<"\n"<<y1;
float n1=pow(N,y1);
// float y2=pow(y,N);
// float n2=pow(N,b);

float cl=O*S*D*f0*p1*N;
cout<<"\n"<<N;
cout<<"\nlabour cost"<<cl;

float csl=0.15*cl;
cout<<"\nsupervision charges"<<csl;

float cola=cl;
cout<<"\n overall,laboratory,administrative"<<cola;
//fixed charges
float cfc=a*N*(F+f)*pfc;
out<<"\nfixed cost"<<cfc;

float ccwl=885600/n1;
out<<"\ncondenser and cooling water cost"<<ccwl;

//
float mvn=(mvi*3600)/n1;
out<<"\n"<<mvn;
float mcw=(mvn*(hvn-cpw*t2))/(cpw*(t2-t1));
float ccw=mcw*pcw;
out<<"\n"<<mcw;out<<"\n cooling water cost"<<ccw;

//steam charges

```

```

float cs=(mvi*3600)*ps*24*f0/n1;//cs=31185e+04/n1;//
out<<"\nsteam cost"<<cs;

//
float cc=(k1*Cc*D1*a*((N-2)+2/k1))/R;
out<<"\ncleaning cost"<<cc;

//
float cmr=cfc*f;
out<<"\nrepair maintenance cost"<<cmr;

//
float e=(mvn*w)/vstd;
float cce=pic*(F+f)*pow(e,0.6);
out<<"\nequipment cost for condensing, injection"<<cce;

//
float e1=(1.43*mvi*a1/24)+(mvn*w*a5/24);
float cae=pastd*(F+f)*pow(e1,0.6)*(pow(1/vstd,0.6));
out<<"\ncost for air handling equipment"<<cae;

//
float cp=mvn*D*w*f0*(cpi+cpa+cpc+rcw);
out<<"\noperating power cost for condensing,cooling,injection and air
handling"<<cp;

//
float cbpr=28*p1*pow(N,b)*(F+f);
out<<"\ncost due to BPR"<<cbpr;

total cost
float ct=cl+csl+cola+cfc+cs+ccw+cc+cmr+cce+cae+cbpr+cp;
out<<"\n"<<ct;

getch();
} } //end of main

```


/*PROGRAM TO ESTIMATE CHEMICAL CONSUMPTION (NaOH) DUE TO CARRYOVER SOLIDS WITH PULP*/

```

#include<fstream.h>
#include<conio.h>
void main()
{
float x,y,z,Mcl,Mc,Mlig,Mna,Mhcl,N,fr,C;
ifstream inn("inp.txt");
// cout<<"\n enter total solid going with the pulp;";
inn>>x;
// cout<<"\n enter %lignin:";
inn>>y;
// cout<<"\n enter %carbohydrates:";
inn>>z;
// cout<<"\n enter molecular weight of chlorine:";
inn>>Mcl;
// cout<<"\n enter molecular weight of lignin:";
inn>>Mlig;
// cout<<"\n enter molecular weight of hydrochloric acid:";
inn>>Mhcl;
// cout<<"\n enter molecular weight of carbohydrate:";
inn>>Mc;
// cout<<"\n enter molecular weight of sodium hydroxide:";
inn>>Mna;
// cout<<"\n enter washing efficiency:";
inn>>N;
// cout<<"\n enter fraction of applied Cl2 to generate HCl:";
inn>>fr;
// cout<<"\n enter cost of sodium hydroxide Rs/kg;";
inn>>C;

float Lc=x*y;
cout<<"\n lignin content, kg/ton:"<<Lc;
float Cc=x*z;
cout<<"\n carbohydrates, kg/ton:"<<Cc;
float Cls=(Mcl/Mlig)*Lc;
cout<<"\n chlorine consumption, kg/ton:"<<Cls;
float AClS=Cls/fr;
cout<<"\n applied chlorine, kg/ton:"<<AClS;
float HClS=(Mhcl/Mcl)*AClS;
cout<<"\n HCl generated in substitution of lignin, kg/ton:"<<HClS;
float HClO=2*HClS;
cout<<"\n HCl generated in oxidation of lignin, kg/ton:"<<HClS;
float Cco=(Mcl/Mc)*Cc;
cout<<"\n chlorine consumption in oxidation of carbohydrates:"<<Cco;
float ACco=Cco/fr;
cout<<"\n applied chlorine in oxidation of carbohydrates:"<<ACco;
float HClco=2*(Mhcl/Mcl)*ACco;
cout<<"\n HCl generated in oxidation of carbohydrates:"<<HClco;
float HClT=HClS+HClO+HClco;
cout<<"\n total HCl generated/ton of pulp;"<<HClT;

```

```
float Co=(100-N)/100;
cout<<"\n carry over;"<<Co;
float HCo=HClt*Co;
cout<<"\n carry over, kg Hcl/ton of pulp;"<<HCo;
float NaOH=(Mna/Mhcl)*HClt;
cout<<"\n caustic required to neutralize;"<<NaOH;
float CNaOH=C*NaOH;
cout<<"\n cost of NaOH;"<<CNaOH;
getch();
}
```

```

/* PROGRAM TO ESTIMATE HEAT VALUE OF BLS AND STEAM GENERATION BY
MODIFIED GREEN & GRACE METHOD (BASED ON ALGORITHM-1 (Chap-5)) */
#include <fstream.h>
#include <conio.h>
void main ()
{
float
Pad, Yb, Yup, Lw, ka, Y, Z, V, HVlig, HVmo, HVrf, HVoa, AA, Sl, Cna, rhobl, Tblh, We, Sr, W
, HVi;
ifstream inn("hv.txt");
inn>>Pad; inn>>Yb; inn>>Yup; inn>>Lw; inn>>ka; inn>>Y; inn>>Z; inn>>V; inn>>HVli
g; inn>>HVmo;
inn>>HVrf; inn>>HVoa; inn>>AA; inn>>Sl; inn>>Cna; inn>>rhobl; inn>>Sr; inn>>W; i
nn>>HVi; inn>>We; inn>>Tblh;

float Pod = Pad*0.90;
cout<<"\n bleached pulp, od tons/day:"<<Pod;
float UP=(100*Pod)/Yb;
cout<<"\n unbleached pulp, od tons/day:"<<UP;
float Wo=(100*UP)/Yup;
cout<<"\n wood used, od tons/day:"<<Wo;
float Wup=(Wo*2000)/UP;
cout<<"\n wood used, od lb/od tons:"<<Wup;
float Vup=Wup/100;
cout<<"\n volatiles lost, od lb/od tons:"<<Vup;
float Obl=Wup-2000-Vup;
cout<<"\n organics in BL, od lb/odton up:"<<Obl;
float Lod=(Lw*Wup)/100;
cout<<"\n lignin in wood, od lb/ton up:"<<Lod;
float Lup=3*ka;
cout<<"\n lignin in BL, odlb/odton up:"<<Lup;
float Lbl=Lod-Lup;
cout<<"\n lignin up, od lb/od ton up:"<<Lbl;
float Om=Y*Wup;
cout<<"\n mix organics in BL, od lb/ton up:"<<Om;
float Orf = Z*Wup;
cout<<"\n resins, fatty acids, odlb/odton up:"<<Orf;
float Oto= V*Orf;
cout<<"\n tall oil recovered , od lb/od ton up:"<<Oto;
float RFbl=Orf-Oto;
cout<<"\n resin, fatty acids in BL odlb/od ton up:"<<RFbl;
float Oc= Obl- (Lbl+Om+Orf);
cout<<"\n organics acids from carbohydrates:"<<Oc;
float TO= Lbl+ Om + RFbl + Oc;
cout<<"\n total organics in BL, od lb/od ton up:"<<TO;
float THVlig = Lbl* HVlig /2000;
cout<<"\n heating value of resins fatty acids:"<<THVlig;
float THVmo= Om*HVmo/2000 ;
cout<<"\n heating value mix organics:"<<THVmo;
float THVrf = RFbl*HVrf/2000;
cout<<"\n heating value of resins, fatty acids:"<<THVrf;
float THVoa = Oc*HVoa/2000;
cout<<"\n heating value of organics acids flow carbohydrates:"<<THVoa;

```

```

float HVo=THVlig + THVmo + THVrf + THVoa;
cout<<"\n total heating value of organics in BL:"<<HVo;
float Naa=(AA*Wup)/100;
cout<<"\n aa applied, as Na2O, od lb/od ton up:"<<Naa;
float Ns=Naa*S1/100;
cout<<"\n na2s applied, as na2o,od lb/od ton UP:"<<Ns;
float Nco3= 1.71*(Naa-Ns)*(100-Cna)/Cna;
cout<<"\n na2co3 in wl,od lb/od ton UP:"<<Nco3;
float Nso4=2.29*Ns*(100-Sr)/Sr;
cout<<"\n na2so4 in wl,od lb/od ton UP:"<<Nso4;
float Tino=(1.29*Naa*(1-S1/100))+1.26*Ns+Nco3+Nso4;
cout<<"\n total inorganic solids, od lb/od ton UP:"<<Tino;
float Tbl=TO+Tino-W;
cout<<"\n total BLS,od lb/ od ton UP;"<<Tbl;
float Obls=(TO*100)/Tbl;
cout<<"\n organics in BL,%;"<<Obls;
float THVi=Ns*HVi/1000;
cout<<"\n inorganic heating value,Btu/od ton UP;"<<THVi;
float Hvt=HVo+THVi;
cout<<"\n total heating value, Btu/od ton up;"<<Hvt;
float Hvs=Hvt*1e+6/Tbl;
cout<<"\n solids heating value,Btu/lb BLS;"<<Hvs;
float Tbos=(Tbl*We)/100;
cout<<"\n total BLS to boiler, od lb/od ton up;"<<Tbos;
float Tbol=(Tbl*We)/Tblh;
cout<<"\n total BL to boiler, od lb/od ton up;"<<Tbol;
float FR=(Tbol*UP*7.48)/(1440*rhobl);
cout<<"\n BL firing rate, gal/min;"<<FR;
float Blo=(Hvt*We)/100;
cout<<"\n boiler load,Btu/od ton up;"<<Blo;
float BLO=(Blo*UP)/1440;
cout<<"\n boiler load,Btu/min;"<<BLO;
getch();
}

```

```

/* PROGRAM TO ESTIMATE HEAT VALUE OF BLS AND STEAM GENERATION BASED ON
ALGORITHM-2 (Chap-5) */

```

```

#include<fstream.h>
#include<conio.h>
void main()
{
float bls,e,x,y,z,w,hvl,hvm,hvr,hvo,s,t,hvs,hvso;
ifstream inn("inh.txt");
//cout<<"\n Enter total BLS tonne/tonne of pulp going to
evaporator(1.45):";
cin>>bls;
// cout<<"\n Enter enthalpy per kg of steam delivered(kJ/kg):";
inn>>e;
//cout<<"\n Enter %lignin(.34):";
inn>>x;
//cout<<"\n Enter %misc organics(.0548):";
inn>>y;
//cout<<"\n Enter %resins,fatty acids(.0145):";
inn>>z;
//cout<<"\n Enter %organic acids from carbohydrates(.278):";
inn>>w;
// cout<<"\n Enter %of Na2S as Na2O(.00387):";
inn>>s;
// cout<<"\n Enter %of Na2S2O3 as Na2O(.00542):";
inn>>t;
// cout<<"\n Enter heat value of lignin(26900):";
inn>>hvl;
//cout<<"\n Enter heat value of misc.organics(19352):";
inn>>hvm;
//cout<<"\n Enter heat value of resins,fatty acids(37710):";
inn>>hvr;
// cout<<"\n Enter heat value of organic acids(13555):";
inn>>hvo;
// cout<<"\n Enter heat value of Na2S(12900 Btu/lb):";
inn>>hvs;
// cout<<"\n Enter heat value of Na2S2O3(5790 Btu/lb):";
inn>>hvso;

float lbl=bls*x*1000;
cout<<"\n lignin in BL, od kg/od tonne;"<<lbl;
float om= bls*y*1000;
cout<<"\n misc.organics in BL, od kg/od tonne;"<<om;
float rf=bls*z*1000;
cout<<"\n resins,fatty acids in BL, od kg/od tonne;"<<rf;
float oc=bls*w*1000;
cout<<"\n organic acids from carbohydrates in BL, od kg/od tonne;"<<oc;
float to=lbl+om+rf+oc;
cout<<"\n total organics in BL, od kg/od tonne;"<<to;
float thvl=lbl*hvl;
cout<<"\n total heating value of lignin kJ/od tonne;"<<thvl;
float thvm=om*hvm;
cout<<"\n total heating value of misc.organics,kJ/od tonne;"<<thvm;

```

```

float thvr=rf*hvr;
cout<<"\n total heating value of resins &fatty acids;"<<thvr;
float thvo=oc*hvo;
cout<<"\n total heating value of organic acids from carbohydrates,kJ/c
tonne;"<<thvo;
float Ohv=thvl+thvm+thvr+thvo;
cout<<"\n total heating value of organics in BL;"<<Ohv;

float Ns=bls*s*1000;
cout<<"\n Na2S in BL, od kJ/od tonne;"<<Ns;
float Nso=bls*t*1000;
cout<<"\n Na2S2O3 in BL, od kJ/od tonne;"<<Nso;
float thvs=Ns*hvs;
cout<<"\n total heating value of Na2s,kJ/od tonne;"<<thvs;
float thvso=Nso*hvso;
cout<<"\n total heating value of Na2S2O3,kJ/od tonne;"<<thvso;
float Ihv=thvs+thvso;
cout<<"\n total heating value of inorganics in BL;"<<Ihv;
float hv=Ohv+Ihv;
cout<<"\n total heating value of BL;"<<hv;
//float hs=hv/(1000*bls);
//cout<<"\n heat to steam;"<<hs;
float sm=hv/e;
cout<<"\n steam deliveredto mill;"<<sm;
getch();
}

```

```

C      PROGRAMME FOR MULTIPLE EFFECT EVAPORATOR SYSTEM WITH
C      BACKWARD FEED SEQUENCE [ 6->5->4->3->2->]
C
REAL X(12), F(12), DELTA, XTOL, FTOL, AX(12)
REAL T(6), BPR(7), ALAM(6), CP(7), C(6), HU(6), PR(6)
REAL FLI(7), DELT(7), EVAP(7), AUP(7), ALP(7), BPRP(7), TLP(7)
REAL XF, XP, TO, TF, TN, CPV, FR
INTEGER N, MAXIT, I
COMMON/B1/XF, XP, TO, TF, TN, CPV, FR, ALAMO
COMMON/B2/HU, BPR, ALAM, CP, C, T, PR
EXTERNAL FCN
DATA I, N, NE, MAXIT, DELTA/0, 12, 6, 20, 0.01/
DATA XTOL, FTOL/0.0001, 0.0005/
C      DATA X, XTOL, FTOL/0.467, 0.589, 0.696, 0.787, 0.863, 0.872, 0.773,
C      10.677, 0.593, 0.512, 0.143, 1.13, 0.0001, 0.0005/
DATA X/0.479, 0.583, 0.688, 0.792, 0.896, 0.896, 0.792,
1 0.688, 0.583, 0.479, 2.0, 1.13/
C      DATA X/0.397, 0.518, 0.638, 0.796, 0.921, 0.892, 0.784, 0.676,
C      1 0.568, 0.460, 2.0, 1.13/
      DO 99 K=1, 12
      AX(K)=X(K)
99  CONTINUE
C      FR=190308.37
      XP=0.50
      CPV=0.50
      HU(1)=262
      HU(2)=295
      HU(3)=252
      HU(4)=251
      HU(5)=221
      HU(6)=221
      OPEN (UNIT=11, FILE='XF.DAT')
      OPEN(UNIT=12, FILE='MSOUT2.DAT')
      DO 21 LP1=1, 8
      READ (11, *) TO, TF, TN, XF, FR
C      TO=282.2
C      TF=176.0
C      TN=120.2
C      XF=0.15
      N1=NE-1
      DO 20 IKL=1, 20
      CALL NLSYST(FCN, N, NE, MAXIT, X, F, DELTA, XTOL, FTOL, I)
C
C      DETERMINATION OF OVERALL HEAT TRANSFER COEFFICIENT
C
      DO 111 J=1, N1
      ALP(J+1)=X(J)
      AUP(J)=X(J+N1)
111  CONTINUE
      AUP(NE)=TN/TO
      AUP(NE+1)=TF/TO
      ALP(1)=XF/XP
      DO 112 I=1, NE

```

```

AUP(I)=AUP(I)*TO
ALP(I)=ALP(I)*FR
BPRP(I)=BPRP(I)*TO
TLP(I)=BPRP(I)+AUP(I)
112 CONTINUE
DO 113 M=1,N1
FLI(M)=ALP(M+1)
DELT(M+1)=AUP(M)-TLP(M+1)
EVAP(M)=ALP(M+1)-ALP(M)
113 CONTINUE
FLI(NE)=FR
DELT(1)=TO-TLP(1)
EVAP(NE)=FR-ALP(NE)
ST2=X(N)*(FR/50.)
TLP(NE+1)=TF
C(NE+1)=XF
DO 114 IJ=1,NE
CALL HTC(C(IJ),TLP(IJ),TLP(IJ+1),OHTC,FLI(IJ),EVAP(IJ),ALAM(IJ
1,ST2)
HU(IJ)=OHTC
C WRITE(*,*)'IJ=',IJ
114 CONTINUE
C WRITE(*,*)'IKL=',IKL
C WRITE(*,*)'X',(X(KL),KL=1,12)
C WRITE(*,*)'F',(F(KL),KL=1,12)
20 CONTINUE
CALL TABLE(X,N,NE)
21 CONTINUE
STOP
END

C -----
SUBROUTINE FCN (X,F,N,NE)
C -----
C SUBROUTINE FCN FOR AUTOMATIC GENERATION OF MASS AND ENERGY
C BALANCE EQUATIONS FOR MULTI EFFECT EVAPORATOR SYSTEMS
C XF: INITIAL CONCENTRATION OF FEED
C XP: FINAL CONCENTRATION OF PRODUCT
C TO: STEAM TEMPERATURE
C TF: FEED TEMPERATURE
C TN: TEMPERATURE OF Nth BODY
C F : FEED FLOW RATE
C NE: NO OF EFFECTS
C AU: SCALED TEMPERATURES OF EFFECTS
C AL: SCALED FLOW RATE OF EFFECTS
C T : TEMPERATURE OF DIFFERENT EFFECTS
C BPR BOILING POINT RISE( SCALED) IN DIFFERENT EFFECTS
C PL: LATENT HEAT OF VAPORIZATION IN DIFFERENT EFFECTS
C CP: SPECIFIC HEAT OF DIFFERENT EFFECTS
C C : CONCENTRATION OF LIQUOR IN DIFFERENT EFFECTS
C -----
REAL X(12),F(12),T(6),BPR(7),ALAM(6),CP(7),C(6),AL(7)
REAL AU(7),HU(6),PR(6)
REAL XF,XP,TO,TF,TN,CPV,FR

```



```

COMMON/B1/XF,XP,TO,TF,TN,CPV,FR,ALAMO
COMMON/B2/HU,BPR,ALAM,CP,C,T,PR
N1=NE-1
AU(NE+1)=TF/TO
AL(NE+1)=1.0
AU(NE)=TN/TO
T(NE)=(AU(NE)*TO-32)*(5.0/9.0)
TF1=(TF-32)*(5.0/9.0)
TO1=(TO-32)*(5.0/9.0)
CP(NE+1)=CP2(XF)/4187
ALAMO=ALAM1(TO1)
AL(1)=XF/XP
BPR(NE+1)=0.0
C   WRITE(*,*)'CHECK',ALAMO,AL(1),TF1,TO1
DO 30 KP=1,N1
AL(KP+1)=X(KP)
AU(KP)=X(KP+N1)
T(KP)=(AU(KP)*TO-32)*(5.0/9.0)
30  CONTINUE
DO 40 K2=1,NE
C(K2)=XF/AL(K2)
BPR(K2)=BPR1(C(K2))/TO
CP(K2)=CP2(C(K2))/4187
ALAM(K2)=ALAM1(T(K2))
PR(K2)=PRS(T(K2))
C   WRITE(*,*)'PHY',C(K2),BPR(K2),CP(K2),ALAM(K2),T(K2),PR(K2)
40  CONTINUE
C   -----
C   DEVELOPMENT OF EQUATIONS FOR MULTI EFFECT EVAPORATOR SYSTEM
C   FROM EFFECT NO. 1 TO EFFECT NO. NE
C
C   FOR FIRST EFFECT
C
C   F(1)=TO*AL(2)*(CP(2)*(AU(2)+BPR(2))-CP(1)*(AU(1)+BPR(1)))/ALAMO+
1 X(N-1)-(AL(2)-AL(1))*(ALAM(1)+CPV*BPR(1)*TO)/ALAMO
F(2)=HU(1)*TO*X(N)*(1-(AU(1)+BPR(1)))/(50.*ALAMO)-X(N-1)
C
C   FOR SECOND TO LAST EFFECT(FIXED BY THE VALUE OF NE)
C
C   KL=3
DO 20 J=2,NE
F(KL)=TO*AL(J+1)*(CP(J+1)*(AU(J+1)+BPR(J+1))-CP(J)*(AU(J)+
1 BPR(J)))/ALAMO+(AL(J)-AL(J-1))*(ALAM(J-1)+CPV*BPR(J-1)*TO)/ALAMO
1-(AL(J+1)-AL(J))*(ALAM(J)+CPV*BPR(J)*TO)/ALAMO
F(KL+1)=HU(J)*TO*X(N)*(AU(J-1)-(AU(J)+BPR(J)))/(50.*ALAMO)
1-(AL(J)-AL(J-1))*(ALAM(J-1)+CPV*BPR(J-1)*TO)/ALAMO
KL=KL+2
20  CONTINUE
C
C   -----
C   EQUATION FOR PHYSICO-THERMAL PROPERTIES ARE INCLUDED INTERMS
C   OF FUNCTIONS PL1(T),CP1(CC,T),BPR1(CC)
RETURN

```

```

END
FUNCTION ALAM1(T)
ALAM1=(2519.5-2.653*T)/2.3249
RETURN
END
FUNCTION CP1(CC,T)
T1=T*1.8+32
CP1=(1.0-3.234*(CC/T1))*4190
RETURN
END
FUNCTION BPR1(CC)
BPR1=41.4*(CC+0.1)**2
RETURN
END
FUNCTION PRS(T)
T1=T*1.8+32
PRS=3.73812-0.108896*T1+0.0012806*T1**2-6.69111E-06*T1**3
1+1.99203E-08*T1**4
RETURN
END
SUBROUTINE TABLE(X,N,NE)

```

C
C
C

THIS SUBROUTINE TABULATES THE RESULTS IN TABULAR FORM

```

REAL XF,XP,TO,TF,TN,CPV,FR,ALAMO
REAL X(12),T(6),BPR(7),ALAM(6),CP(7),C(6),AL(7),AU(7),HU(6)
REAL PR(6),TL(6),DELT(6),FLI(6),EVAP(6)
INTEGER N,I, KK(6)
COMMON/B1/XF,XP,TO,TF,TN,CPV,FR,ALAMO
COMMON/B2/HU,BPR,ALAM,CP,C,T,PR
WRITE(12,90)
N1=NE-1
DO 5 K=1,6
KK(K)=K
5 CONTINUE
WRITE(12,180)
WRITE(12,100)(KK(L),L=1,6)
WRITE(12,180)
DO 10 J=1,N1
AL(J+1)=X(J)
AU(J)=X(J+N1)
10 CONTINUE
PLO=PLO*2.323
AU(NE)=TN/TO
AU(NE+1)=TF/TO
AL(1)=XF/XP
DO 20 I=1,NE
AU(I)=(AU(I)*TO-32)*(5.0/9.0)
AL(I)=AL(I)*FR*1.260E-04
BPR(I)=BPR(I)*TO/1.8
TL(I)=BPR(I)+AU(I)
PR(I)=PR(I)*6.895
ALAM(I)=ALAM(I)*2.326

```

```

      HU(I)=HU(I)*5.678
      CP(I)=CP(I)*4.187
20    CONTINUE
      DO 30 M=1,N1
      FLI(M)=AL(M+1)
      DELT(M+1)=AU(M)-TL(M+1)
      EVAP(M)=AL(M+1)-AL(M)
30    CONTINUE
      FR1=FR*1.260E-04
      FLI(NE)=FR1
      DELT(1)=(TO-32)/1.8 -TL(1)
      EVAP(NE)=FR1-AL(NE)
      ST1=X(N-1)*FR1
      ST2=X(N)*(FR/50.)*9.290E-02
      SE=(FR1*(1-XF)-AL(1)*(1-C(1)))/ST1
      TO=(TO-32)*(5.0/9.0)
      TF=(TF-32)*(5.0/9.0)
      TN=(TN-32)*(5.0/9.0)
      WRITE(12,80)(PR(I),I=1,6)
      WRITE(12,110)(AU(I),I=1,6)
      WRITE(12,120)(BPR(I),I=1,6)
      WRITE(12,125)(TL(I),I=1,6)
      WRITE(12,130)(ALAM(I),I=1,6)
      WRITE(12,140)(CP(I),I=1,6)
      WRITE(12,150)(HU(I),I=1,6)
      WRITE(12,155)(DELT(I),I=1,6)
      WRITE(12,157)(FLI(I),I=1,6)
      WRITE(12,160)(AL(I),I=1,6)
      WRITE(12,159)(EVAP(I),I=1,6)
      WRITE(12,170)(C(I),I=1,6)
      WRITE(12,180)
      WRITE(12,190)FR1
      WRITE(12,195)XF,XP
      WRITE(12,200)TO,TF,TN
C      WRITE(12,220)SE
      WRITE(12,205)ST1,ST2
      WRITE(12,210)SE
80    FORMAT(2X,'PRESS ',2X,7(F8.3,2X))
125   FORMAT(2X,'L.TEMP ',2X,7(F6.2,4X))
155   FORMAT(2X,'DELT ',2X,7(F6.2,4X))
157   FORMAT(2X,'L/I ',2X,7(F7.3,3X))
159   FORMAT(2X,'EVAP ',2X,7(F7.3,3X))
90    FORMAT(/2X,'RESULTS FOR MULTI EFFECT EVAPORATOR SYSTEMS'
1/2X,'(EXACTLY BACKWARD FEED PROGRAMME:A2.FOR)'/)
100   FORMAT(2X,'EFFECTS ',2X,7(I2,8X))
110   FORMAT(2X,'S.TEMP ',2X,7(F6.2,4X))
120   FORMAT(2X,'BPR ',2X,7(F6.2,4X))
130   FORMAT(2X,'LAMDA ',2X,7(F8.1,2X))
140   FORMAT(2X,'Sp.HT ',2X,7(F6.4,4X))
150   FORMAT(2X,'H.T.C. ',2X,7(F8.1,2X))
160   FORMAT(2X,'L/O ',2X,7(F7.3,3X))
170   FORMAT(2X,'CONC. ',2X,7(F7.5,3X))
180   FORMAT(2X,76('-'))

```

```

190   FORMAT(2X,'LIQUOR FEED RATE= ',,F8.5)
195   FORMAT(2X,'FEED CONC.          = ',2X,F7.5,2X,
1'PRODUCT CONC.= ',F7.5)
C200   FORMAT(2X,'STEAM CONSUMPTION = ',2X,F10.4,2X,'AREA= 'F10.3)
C220   FORMAT (2X,'STEAM ECONOMY = ',F8.3)
200   FORMAT(2X,'STEAM TEMP.= ',F6.2,2X,'FEED TEMP.=' ,F6.2,2X,'LAST'
1' EFFECT TEMP.= ',F6.2)
205   FORMAT(2X,'STEAM CONSUMPTION=',2X,F10.4,2X,'AREA='F10.3)
210   FORMAT(2X,'STEAM ECONOMY = ',F8.3)
      RETURN
      END

C
      SUBROUTINE HTC(CC,T,TI,OHTC,AL,EVP,ALAMK,ARA1)
      REAL CC,T,TI,OHTC,AL,EVP,ALAMK

C
C   DETERMINATION OF OVERALL HEAT TRANSFER COEFFICIENT FOR LONG TU
C   VERTICAL EVAPORATORS. THE FUNCTIONAL RELATIONSHIP OF OVERALL
C   HEAT TRANSFER COEFFICIENT WITH OTHER OPERATING PARAMETERS ARE
C   GIVEN BELOW:
C
C       p2
C   U=p1.CK . (p3.Q+p4.Q**2+p5.Q**3)
C
C   CK = CAMU*CT*CF

C
C   WHERE p1 TO p5 ARE CONSTANTS.CAMU ACCOUNTS FOR THE CHANGES IN
C   VISCOSITY, CT IS THE CORRECTION FACTOR FOR BOILING POINT AND C
C   IS THE COMBINED CORRECTION FACTOR FOR LIQUID FEED RATE IN
C   COMBINATION WITH LIQUID FEED TEMPERATURE AND HEAT FLUX.
C
C   GEOMETRICAL PARAMETERS:
C
C   LENGTH OF TUBE                : 8.5 m
C   DIAMETER OF TUBE(OUTER)       : 0.051 m
C   DIAMETER OF TUBE(INNER)       : 0.048 m
C   MATERIAL OF CONSTRUCTION      : STAINLESS STEEL SIS 2343
C   THERMAL CONDUCTIVITY OF MATERIAL : 14.6 W/mK ( 70-130 DEG.C)
C
C   DESCRIPTION OF VARIABLES:
C
C   TB      : BOILING POINT OF LIQUOR (TSAT+BPR) DEGREE CELCIUS
C   Q        : HEAT FLUX, W/sq.m
C   FD       : FEED RATE PER PER CROSS SECTIONAL AREA, kg/(s.sq.m)
C   TSUB     : SUBCOOLING OF LIQUID FEED ( TMAX-TIN) DEGREE CELCIUS
C   TSUP     : SUPERHETING OF LIQUOR FEED (TIN-TMAX) DEGREE CELCIUS
C   EVP      : EVAPORATION RATE FROM A BODY
C   PLK      : LATENT HEAT OF VAPORIZATION
C   ANT      : NO.OF TUBES
C   CSANT    : CROSS SECTIONAL AREA OF TOTAL TUBES
C   AL       : LIQUOR FLOW RATE
C   p1-p31   : ADJUSTED CONSTANTS VALUE
C
C   CONVERSION OF UNITS
C   TIN=(TI-32)*0.5555
C   T1=(T-32)*0.5555

```

ALF=AL*1.260E-04
EVA=EVP*1.260E-04
ALAML=ALAMK*2326
ARA=ARA1*9.290E-02

T1,TIN : DEGREE CELCIUS
ALF,EVA : kg/s
PLL : J/kg
ARA : square meter

DETERMINATION OF CORRECTION FACTOR CK (=CAMU*CT*CF)

DETERMINATION OF PHYSICAL PROPERTIES

AMU=1.0E-03*AMU1(CC,T1)
CP=CP2(CC)
RHO=RHO1(CC,T1)
THERC=THERC1(CC,T1)
WRITE(*,*)'AMU,CP,RHO,THERC,T1,TIN,ALF,EVA,ALAML,ARA',AMU,CP,RHO,
1THERC,T1,TIN,ALF,EVA,ALAML,ARA

L1=0
TB=T1

DETERMINATION OF FD VALUE AND HEAT FLUX

ANT=ARA/(8.5*3.14*0.051)
CSANT=3.14*(0.048/2)**2*ANT
FD=ALF/CSANT
Q=EVA*ALAML/ARA
DETERMINATION OF CORRECTION FACTOR, CAMU
p1=0.981
p2=1.00
p3=0.2334
p4=-0.1006E-04
p5=0.1362E-09
p6=1.00
p7=-0.07858
p8=0.002735
p9=-0.1092E-05
p10=-1.02
p11=0.0467
p12=-0.364E-03
p13=0.946E-06
p14=-0.0515
p15=0.0505
p16=0.01
p17=21800.0
p18=0.40
p19=19500.0
p20=2000.0
p21=-95.0
p22=150.0
p23=0.12

```

p24=-0.001
p25=3.0
p26=-0.025
p27=-0.12
p28=4300.0
p29=100.0
p30=-14.0
p31=0.04
C
IF (AMU.GT.0.OR.AMU.LE.15) THEN
CAMU=p6+p7*AMU+p8*AMU**2+p9*AMU**3
ENDIF
IF (AMU.GT.15) CAMU=1.576-0.095*LOG10 (AMU)
C
C
C DETERMINATION OF CORRECTION FACTOR, CT
C
CT=p10+p11*TB+p12*TB**2+p13*TB**3
C DETERMINATION OF FACTOR, CF
C
TMAX =p22+(p23+p24*TB) *FD+(p25+p26*TB) *LOG10 (AMU)+p27*TB
TSUB=TMAX-TIN
IF (TSUB.LT.0) L1=1
IF (TSUB.LT.0) TSUB=0.0
IF (AMU.LT.1.0) AMUC=1.0
IF (AMU.GE.1.0) AMUC=AMU
C WRITE (*, *) 'TSUB, TMAX, Q, FD, ANT, ALF, CSANT', TSUB, TMAX, Q, FD, ANT, AI
C 1CSANT
C
C CALCULATION OF HEAT FLUX BOUNDS
C
BOUND1=p19+p20*LOG10 (AMUC)+p21*TB
BOUND2=p28+p29*LOG10 (AMUC)+p30*TB
C WRITE (*, *) 'BOUND1, BOUND2', BOUND1, BOUND2
C
IF (TSUB.EQ.0) THEN
Z=1.0
GO TO 33
ENDIF
Z=1.0+p16* (TANH ((Q-BOUND1) /p17)) *TSUB**p18
33 CONTINUE
CF=Z+(p14+p15*Z) *FD
CK=CAMU*CT*CF
C WRITE (*, *) 'Z, CAMU, CT, CF, CK', Z, CAMU, CT, CF, CK
C
C DETERMINATION OF ADDED HEAT FLUX DUE TO SUPER HEATING OF LIQUI
C FEED, DELQ
C
IF (L1.EQ.1) GO TO 10
GO TO 20
10 CONTINUE
TSUP=TIN-TMAX

```

```

                DELQ=TSUP*CP*FD*(3.14*(0.0048**2)/4.)/1.321
20      CONTINUE
C
C      DETERMINATION OF OVERALL HEAT TRANSFER COEFFICIENT IF THE VALUE OF
C      Q LIES BETWEEN 0 TO 20000 W/sq.m
C
                Q1=Q+DELQ
                IF(Q1.GT.20000)Q1=20000
                IF(Q1.GT.0.0.AND.Q1.LE.20000)THEN
                OHTC=p1*(CK*p2)*(p3*Q1+p4*Q1**2+p5*Q1**3)
                ENDIF
                OHTC=OHTC/5.678
C      WRITE(*,*)'TSUP,Q1,OHTC,DELQ',TSUP,Q1,OHTC,DELQ
C
C      AT EXTREMELY LOW HEAT FLUXES GIVEN BY Q < BOUND2 THE METHODOLOGY
C      FOR DETERMINATION OF OVERALL HEAT TRANSFER COEFFICIENT DIFFERS
                IF(Q1.LE.BOUND2)THEN
C      WRITE(*,30)Q1,BOUND2
                ENDIF
                GO TO 50
                IF(Q1.GT.BOUND2)GO TO 40
                IF(Q1.LE.BOUND2)THEN
C      WRITE(*,30)BOUND2
                ENDIF
                VOL=FD/RHO
                REN=0.048*VOL*RHO/AMU
                PRN=CP*AMU/THERC
                H1=0.023*REN**0.8*PRN**0.4*THERC/0.048
                Q2=BOUND2
                HTC=0.981*(CK**1.0)*(0.2334*Q2-0.1006E-04*Q2**2+0.1362E-
109*Q2**3)
                CSUB=1.0+p31*TSUB*((BOUND2-Q1)/BOUND2)**2
                OHTC=(H1+(HTC-H1)*Q1/BOUND2)*CSUB
C      WRITE(*,*)'OHTC,VOL,REN,PRN,H1,CSUB,HTC','OHTC,VOL,REN,PRN,H1,
C      1CSUB,HTC
40      CONTINUE
50      CONTINUE
30      FORMAT(2X,'Q= ',F8.1,'< BOUND2=',F8.1,' RESULTS DOUBTFUL')
                RETURN
                END
C=====
C      DETERMINATION OF VISCOSITY,SPECIFIC HEAT,DENSITY AND
C      THERMAL CONDUCTIVITY OF BLACK LIQUOR
C-----
C      AMU  = VISCOSITY, Kg/sm*1.00E03 OR CENTI POISE
C      CP   = SPECIFIC HEAT, Ws/kgK
C      RHO  = DENSITY ,kg/Cube meter
C      THERC= THERMAL CONDUCTIVITY, W/mK
C      T    =TEMPERATURE OF LIQUOR DEGREE CELCIUS
C      C1   =TOTAL SOLID CONTENT IN BLACK LIQUOR, %
C      CC   =TOTAL SOLID CONTENT IN LIQUOR,MASS FRACTION
C-----
C

```

```

FUNCTION AMU1 (CC,T)
C1=CC*100
A =0.4717-0.02472*T+0.7059E-05*T**2
B =0.06973-0.5452E-03*T+0.1656E-05*T**2
C =0.002046+0.3183E-04*T-0.9761E-07*T**2
D =0.5793E-04-0.6129E-06*T+0.1837E-08*T**2
E =A+B*C1+C*C1**2+D*C1**3
AMU1=EXP(E)
RETURN
END

```

```

C-----
FUNCTION CP2(CC)
C1 = CC*100
CP2=(1.0-0.0054*C1)*4187
RETURN
END

```

```

C-----
FUNCTION RHO1(CC,T)
C1 =CC*100
RHO1=1007-0.495*T+6.0*C1
RETURN
END

```

```

C-----
FUNCTION THERC1(CC,T)
THERC1=0.504-0.282*CC+1.35E-03*T
THERC1=THERC1*1.163
RETURN
END

```

```

C=====
SUBROUTINE NLSYST(FCN,N,NE,MAXIT,X,F,DELTA,XTOL,FTOL,I)

```

```

C-----
C SUBROUTINE NLSYST :
C THIS SUBROUTINE SOLVES A SYSTEM OF NON-LINEAR EQUATIONS BY
C NEWTON'S METHOD. THE PARTIAL DERIVATIVES OF THE FUNCTIONS ARE
C ESTIMATED BY DIFFERENCE QUOTIENTS WHEN A VARIABLE IS PERTURBED
C BY AN AMOUNT EQUAL TO DELTA( DELTA IS ADDED). THIS IS DONE FOR
C EACH VARIABLE IN EACH FUNCTION. INCREMENTS TO IMPROVE THE
C ESTIMATES FOR THE X-VALUES ARE COMPUTED FROM A SYSTEM OF
EQUATIONS

```

```

C USING SUBROUTINE ELIM.

```

```

C-----
C PARAMETERS ARE:
C FNC : SUBROUTINE THAT COMPUTES VALUES OF THE FUNCTION
C MUST BE DECLARED EXTERNAL IN THE CALLING PROGRA
C N : THE NUMBER OF EQUATIONS
C MAXIT : LIMIT TO THE NUMBER OF ITERATIONS THAT WILL BE
USED
C X : ARRAY TO HOLD THE X VALUES. INITIALLY THIS ARR
C HOLDS THE THE INITIAL GUESSES. IT RETURNS THE
FINAL VALUES.
C F : AN ARRAY THAT HOLDS THE VALUES OF THE FUNCTION
C DELTA : A SMALL VALUE USED TO PERTURB THE X VALUES SO
PARTIAL

```



```

C          DERIVATIVES CAN BE COMPUTED BY DIFFERENCE QUOTIENT.
C      XTOL          : TOLERANCE VALUE FOR CHANGE IN X VALUES TO STOP
ITERATION,
C          WHEN THE LARGEST CHANGE IN ANY X MEETS XTOL, THE
SUBROUTINE
C          TERMINATES
C      FTOL          : TOLERANCE VALUE ON F TO TERMINATE. WHEN THE
LARGEST F
C          VALUE IS LESS THAN FTOL, SUBROUTINE TERMINATE.
C      I            : RETURNS VALUES TO INDICATE HOW THE SUBROUTINE
TERMINATED
C      I=1          : XTOL WAS MET
C      I=2          : FTOL WAS MET
C      I=-1         : MAXIT EXCEEDED BUT TOLERANCES NOT MET
C      I=-2         : VERY SMALL PIVOT ENCOUNTERED IN GAUSSIAN
ELIMINATION
C          STEP-NO RESULTS OBTAINED
C      I=-3         : INCORRECT VALUE OF N WAS SUPPLIED- N MUST BE
BETWEEN
C          2 AND 10

```

```

-----
REAL X(N), F(N), DELTA, XTOL, FTOL
INTEGER N, MAXIT, I
REAL A(12,13), XSAVE(12), FSAVE(12)
INTEGER NP, IT, IVBL, ITEST, IFCN, IROW, JCOL

```

```

C
C      CHECK VALIDITY OF VALUES OF N
C
IF(N.LT.2.OR.N.GT.12) THEN
I=-3
WRITE(*,1004) N
RETURN
END IF

```

```

-----
C      BEGIN ITERATIONS-SAVE X VALUES, THEN GET F VALUES
C

```

```

NP=N+1
DO 100 IT=1, MAXIT
DO 10 IVBL=1, N
XSAVE(IVBL)=X(IVBL)
10 CONTINUE
CALL FCN(X, F, N, NE)

```

```

-----
C      TEST F VALUES AND SAVE THEM
C

```

```

ITEST=0
DO 20 IFCN=1, N
IF(ABS(F(IFCN)).GT.FTOL) ITEST=ITEST+1
FSAVE(IFCN)=F(IFCN)

```

```

20 CONTINUE
   IF(I.EQ.0) THEN
   WRITE(*,1000) IT,X
   WRITE(*,1001) F
   END IF
C
C -----
C SEE IF FTOL IS MET. IF NOT, CONTINUE. IF SO, SET I=2 AND RETURN
C IF(ITEST.EQ.0) THEN
C   I=2
C   RETURN
C   END IF
C -----
C THIS DOUBLE LOOP COMPUTES THE PARTIAL DERIVATIVES OF EACH FUNCT
C FOR EACH VARIABLE AND STORES THEM IN A COEFFICIENT ARRAY.
C   DO 50 JCOL=1,N
C     X(JCOL)=XSAVE(JCOL)+DELTA
C     CALL FCN(X,F,N,NE)
C     DO 40 IROW=1,N
C       A(IROW,JCOL)=(F(IROW)-FSAVE(IROW))/DELTA
40 CONTINUE
C
C   RESET X VALUES FOR NEXT COLUMN OF PARTIALS
C
C   X(JCOL)=XSAVE(JCOL)
50 CONTINUE
C -----
C NOW WE PUT NEGATIVE OF F VALUES AS RIGHT AND SIDES AND CALL EL
C DO 60 IROW=1,N
C   A(IROW,NP)=-FSAVE(IROW)
60 CONTINUE
C   CALL ELIM(A,N,NP,12)
C
C -----
C BE SURE THAT THE COEFFICIENT MATRIX IS NOT TOO ILL CONDITIONED
C DO 70 IROW=1,N
C   IF(ABS(A(IROW,IROW)).LE.1.0E-6) THEN
C     I=-2
C     WRITE(*,1003)
C     RETURN
C   END IF
70 CONTINUE
C
C -----
C APPLY THE CORRECTIONS TO THE X VALUES, ALSO SEE IF XTOL IS MET
C ITEST=0
C DO 80 IVBL=1,N
C   X(IVBL)=XSAVE(IVBL)+A(IVBL,NP)

```

```

      IF (ABS(A(IVBL, NP)) .GT. XTOL) ITEST=ITEST+1
80  CONTINUE
C
C -----
C  IF XTOL IS MET, PRINT LAST VALUES AND RETURN , ELSE DO ANOTHER
C  ITERATION
C  IF (ITEST.EQ.0) THEN
C    I=1
C    IF (I.EQ.0) WRITE(*,1002) IT,X
C    RETURN
C  END IF
100  CONTINUE
C
C -----
C  WHEN WE HAVE DONE MAXIT ITERATIONS, SET I=-1 AND RETURN
C
C    I=-1
C    RETURN
1000  FORMAT('  AFTER ITERATION NUMBER',I3,'  X AND F VALUES ARE'
1/12F6.3)
1001  FORMAT(12F6.3)
1002  FORMAT('  AFTER ITERATION NUMBER',I3,'  X VALUES (MEETING',
1'  XTOL) ARE'/12F6.3)
1003  FORMAT('  CANNOT SOLVE SYSTEM. MATRIX NEARLY SINGULAR')
1004  FORMAT('  NUMBER OF EQUATIONS PASSED TO NLSYST IS INVALID.',
1'  MUST BE 1<N<11. VALUE WAS ',I3)
      END

      SUBROUTINE ELIM(AB,N, NP,NDIM)
C -----
C  SUBROUTINE ELIM:
C  THIS SUBROUTINE SOLVES A SET OF LINEAR EQUATIONS AND GIVES AN
C  LU DECOMPOSITION OF THE COEFFICIENT MATRIX. THE GAUSS ELIMINATION
C  METHOD IS USED, WITH PARTIAL PIVOTING. MULTIPLE RIGHT HAND SIDED
C  ARE PERMITTED, THEY SHOULD BE SUPPLIED AS COLUMNS THAT AUGMENT THE
C  COEFFICIENT MATRIX.
C -----
C  PARAMETERS ARE:
C  AB      : COEFFICIENT MATRIX AUGMENTED WITH R.H.S. VECTORS
C  N       : NUMBER OF EQUATIONS
C  NP      : TOTAL NUMBER OF COLUMNS IN THE AUGMENTED MATRIX
C  NDIM    : FIRST DIMENSION OF MATRIX AB IN THE CALLING PROGRAMME
C
C  THE SOLUTION VECTOR(S) ARE RETURNED IN THE AUGMENTATION COLUMNS
C  OF AB
C -----
C
C
C  REAL AB(NDIM, NP)
C  INTEGER N, NP, NDIM
C  REAL SAVE, RATIO, VALUE
C  INTEGER NM1, IPVT, IP1, J, NVBL, L, KCOL, JCOL, JROW
C

```

```

C -----
C
C   BEGIN THE REDUCTION
C
C   NM1=N-1
C   DO 35 I=1,NM1
C
C   FIND THE ROW NUMBER OF THE PIVOT ROW. WE WILL THEN INTERCHANGE
C   ROWS TO PUT THE PIVOT ELEMENT ON THE DIAGONAL.
C
C   IPVT=I
C   IP1=I+1
C   DO 10 J=IP1,N
C   IF (ABS (AB (IPVT, I)) .LT. ABS (AB (J, I))) IPVT=J
10  CONTINUE
C
C -----
C   CHECK FOR A NEAR SINGULAR MATRIX
C
C   IF (ABS (AB (IPVT, I)) .LT. 1.0E-6) THEN
C   WRITE (*,100)
C   RETURN
C   END IF
C
C   NOW INTERCHANGE, EXCEPT IF THE PIVOT ELEMENT IS ALREADY ON THE
C   DIAGONAL, DON'T NEED TO
C
C   IF (IPVT.NE.I) THEN
C   DO 20 JCOL=1,NP
C   SAVE=AB (I, JCOL)
C   AB (I, JCOL) =AB (IPVT, JCOL)
C   AB (IPVT, JCOL) =SAVE
20  CONTINUE
C   END IF
C
C -----
C   NOW REDUCE ALL ELEMENTS BELOW THE DIAGONAL IN THE I-TH ROW.
C   CHECK FIRST TO SEE IF A ZERO ALREADY PRESENT. IF SO, CAN SKIP
C   REDUCTION ON THAT ROW.
C
C   DO 32 JROW=IP1,N
C   IF (AB (JROW, I) .EQ. 0) GO TO 32
C   RATIO = AB (JROW, I) /AB (I, I)
C   AB (JROW, I) =RATIO
C   DO 30 KCOL=IP1,NP
C   AB (JROW, KCOL) =AB (JROW, KCOL) -RATIO*AB (I, KCOL)
30  CONTINUE
32  CONTINUE
35  CONTINUE
C
C -----
C   WE STILL NEED TO CHECK AB (N, N) FOR SIZE

```

```

      IF (ABS (AB (N, N)) .LT. 1.0E-6) THEN
      WRITE (*, 100)
      RETURN
      END IF
C
C -----
C NOW WE BACK SUBSTITUTE
C
      NP1=N+1
      DO 50 KCOL=NP1, NP
      AB (N, KCOL) =AB (N, KCOL) /AB (N, N)
      DO 45 J=2, N
      NVBL=NP1-J
      L=NVBL+1
      VALUE=AB (NVBL, KCOL)
      DO 40 K=L, N
      VALUE=VALUE-AB (NVBL, K) *AB (K, KCOL)
40 CONTINUE
      AB (NVBL, KCOL) =VALUE/AB (NVBL, NVBL)
45 CONTINUE
50 CONTINUE
      RETURN
C
100 FORMAT (' SOLUTION NOT FEASIBLE. A NEAR ZERO PIVOT',
1 ' WAS ENCOUNTERED. ')
      END

```

APPENDIX-XI

NOMENCLATURE

- A = Surface area of drum, m^2 (chap-2)
a=Fractional heating area of the effect defined by $a_j = A / (50.F)$, sm^2/kg
A=Heat transfer area of effect, m^2 (chap-3)
a1=Dissolved air in the feed, kg/kg
a5=The air from condensing, injection water, kg/kg
AA =Active alkali % Na_2O on wood,
ABC/(1+BC)= Langmuir adsorption isotherm
 $a_i, b_i, c_i, d_i, e_i, f_i, g_i, h_i, j_i, a_{ij}$ =Coefficient(chap-4)
b=An exponent factor, (chap-3)
BHV =Calorimetric (Bomb) heat value
BLS =Total BLS / t of Pulp going to evaporator or recovery, t/t of pulp
 B_n = Brightness from n^{th} stage, %GE
BPR=Boiling point rise, $^{\circ}C$
 ΔB_1 = Extracted kappa number
 ΔB_2 = Brightness
 ΔB_3 =Residual chemical
C= Carbon in the black liquor solids,% (chap-5)
C=Condensate from steam chest ; Cost; π_i , water injection separated handling :]
spray cooling water. Rs/kg of water
 C_0 = Base cost of bleaching
 C_1 = Price of chlorine in stage 1 and caustic in stage 2 ,Rs/kg
 C_2 = Price of chlorine dioxide in stage 3,Rs/kg
 C_3 = Price of chlorine dioxide in stage 5 and caustic in stage 4,Rs/kg
 C_4 = Price of steam in stages 1 and 2 times the conversion of steam use to temperatu
change, Rs/ $^{\circ}C$
 C_5 = Price of steam in stage 3 times the conversion of steam use to temperature chan
in stage 3, Rs/ $^{\circ}C$
 C_6 = Price of steam in stage 4 and 5 times the conversion of steam use to temperatu
change , Rs/ $^{\circ}C$
CAA =Active alkali concentration, kg/m^3 ,
 C_{Na} =Causting, $NaOH / (NaOH + Na_2CO_3)$, Na_2O %
 C_{sl} =Concentration of the pulp slurry, kg/m^3
 C_y = Pulp consistency, kg of fiber / kg of liquor
 C_{yi} =Inlet vat consistency of pulp, kg of fibers/kg of liquor
D=Number of working days per year exclusive of cleaning days
 e_1 =Evaporation coefficients, $kg/hr m^2$
 E_T =Total amount of water evaporated per day in the evaporator. kg/ day
 f, ψ = Fractional submergence of drum(chap-2)
f =Fraction of first cost for repairs and maintenance per annum (chap-3)
F=Liquor feed rate, kg/s ; fixed charges as fraction of the capital cost of evaporator
 f_0 =Operating factor
Fr=Fraction of applied Cl_2 to generate HCl

$H_{i,s}$ = Wt.percent of element in BLS, %of BLS
 H = The total enthalpy, kJ/mol(Chap-5)
 h = Specific enthalpy of liquor kJ/kg
 H = Specific enthalpy of the vapour, kJ/kg(chap-3)
 HHV = higher heating value of BLS, kJ/kg
 HV_{lig} = Heating value of lignin, kJ/kg
 HV_{M0} = Heating value of miscellaneous organics, kJ/kg
 HV_{OA}, HV_{oa} = Heating value of organic acids, kJ/kg
 $HV_{r,f}$ = Heating value of resins, fatty acids, kJ/kg
 HV_S = Heating value of Na_2S , kJ/kg
 HV_{SO} = Heating value of $Na_2S_2O_3$, kJ/kg
 ΔH = The isothermal heat of formation
 ΔH_{agr} = Latent heat of fusion or evaporation
 ΔH_S = Heat of solution and dilution.
 $J = 1/\sqrt{n}$
 j = A factor used in replacement.
 K = Permeability constant of cake, m^2
 k = adiabatic exponent = c_p/c_v
 k_1 = Mass transfer coefficient, 1/s
 K_1 = Relative cost factor of cleaning ; i , for any body
 $l(z)$ = Arbitrary cake thickness, m
 L = Cake thickness, m(chap-2) and Amount of liquor, kg liquor/kg of pulp(material balance, chap-2)
 L = Liquor flow rate from the effect, Kg/s(chap-3)
 L_w = Lignin in wood, %
 m = Mass of wet cake / Mass of dry cake, kg / kg(chap-2)
 M = A constant(chap-3)
 M_C = Molecular weight of carbohydrate
 M_{Cl} = Molecular weight of chlorine
 M_{HCl} = Molecular weight of HCl
 M_{lig} = Molecular weight of lignin
 M_{NaOH} = Molecular weight of NaOH
 m_p = Mass of particles deposited in filter per unit volume of filtrate, kg/m^3
 N = Speed of the drum, rpm / 60, 1/s
 n = Number of effects in the set (chap-3)
 N_2 = Level of the slurry in the drum, m,
 NHV = net heating value of BLS, kJ/kg
 O = Number of workers per shift
 P = Applied pressure, Pascal
 P_1 = First cost of heating surface area including fabrication and installation charges, Rs.
 p_1 and p_2 = Initial and final pressure of the gas(N/m^2)
 P_{ad} = Bleached pulp, ad t/day
 P_{cw} = Price of cooling water, Rs.
 P_{FC} = Price of heating surface area, Rs.
 P_s = Price for steam, Rs.
 ΔP = Applied vacuum, N / m^2
 $(P_a)_{std}$ = First cost of air handling equipment of some basic capacity (a_{std}) taken as standard.

$(P_a)_{std}$ = First cost of air handling equipment of some basic capacity (a_{std}) taken standard.
 $(P_i + P_c)_{std}$ = Price of a standard pump capable of pumping V_{std} . Amount of water per ho
Rs.
 Q = Rate of heat transfer across the tube from the steam/ water vapour to the liquor, w
 R = Radius of the drum, m(chap-2)
 r = A factor for replacement cum make up water
 R = Time between successive cleaning (for first the two bodies), days(chap-3)
 R_0'' = Vertical distance between drum and vat, m
 R_1 = solids reduction ratio of stage 1.
 R_{a+1-m} = product of solids reduction ratios for stages (a+1) through m
 R_b = ratio of undiluted blow liquor to liquor in sheet liquor from washer
 R_e = ratio of liquor in sheet from washer to liquor to evaporators
Reduction = sulphur reduction efficiency, %
 R_g = ratio of shower liquor in the sheet from washer to total shower liquor
 r_n = chemical residual in n^{th} stage, kg/t of pulp
 R_s = ratio of liquor in the sheet from washer to liquor in shower
 R_v = ratio of liquor in the sheet from washer to liquor in vat
 S = solids in the sheet leaving any given stage, %(chap-2)
 S = black liquor dry solids content, %(Chap-5)
 S = Number of shifts per day(chap-3)
 S_0 = Specific surface of the fiber per volume unit m^2 / m^3
 s_1 = residence time in Ist and IInd stage, min
 s_1 = residence time in VIth and Vth stage, min
 S_1 = solids in liquor from stock leaving stage 1, %
 S_2 = solids in liquor from stock leaving stage 2, %
 s_3 = residence time in IIIrd stage, min
 S_a = solids in the sheet leaving intermediate stage, %
 S_b = solids in the blow, %
 SC = Steam consumption, kg/s
 S_{cc} = salt cake charge
 S_{cl} = salt cake loss
 S_e = Solid to evaporator, %
 SE = Steam economy, kg/kg
 SL = Sulfidity of WL, % of AA,
 S_m = Solids in liquor from stock leaving stage m (final stage), %
 S_r = Sulfur reduction in WL, % ,
 S_s = Solids in the shower liquor, any given stage, %
 S_v = Solids in the vat liquor, %
 S_{WL} = Solids in WL, %
 T = Saturation temperature of water at pressure P , °C
 T_{BLH} = Total BLS is heavy BL, % od lb/od t,
 TS = Total soild content of liquor, %
 u = pH of stage n
 U = $Na_2S_2O_3$ in black liquor, %(chap-5)
 U = Overall heat transfer coefficient, W/m^2k (chap-3)
 v = Tall oil recovered %,
 V = Filtrate volume, m^3 (Cha-2)

V = Vapour flow rate from the effect, kg/s(chap-3)
 v_1 = Specific volume of gas in the initial conditions i.e. at a pressure of p_1 and a temperature of T_1 , (m^3/kg)
 V_f = Filtrate flow rate through cake formation zone, m^3/s
 V_{std} = Standard vapor load, $m^3/hour$
 w = Organic acids from carbohydrates %,
 W = Water formed, t / od t UP(chap-5)
 W = Amount of water required per kg of vapour condensed, kg/kg(chap-3)
 w_1 = extracted kappa number
 w_2 = brown stock kappa number
 W_{ad} = Theoretical amount of work done, J/kg
 W_c = washing efficiency %,
 W_p = weight of liquor in pulp leaving washer per weight of pulp, kg/kg
 W_s = Liquor from shower
 W_{ts} = Total shower liquor
 X = lignin, % (chap-5)
 X = Mass fraction of solute in the liquor(chap-3), Dissolved solids, %(material balance, chap-2)
 x_1 = chemical used in Ist and IInd stage, kg/t of pulp
 X_1 = previous stage kappa number or brightness
 X_2 = chemical addition, kg
 x_3 = chemical usage in stages 3, kg/t of pulp
 X_3 = tower temperature, $^{\circ}C$
 X_4 = residence time
 x_5 = chemical usage in stages 4 and 5, kg/t of pulp
 X_5 = pH
 X_i = Mass of fibers/liquor in the vat $C_{yi}/(1-C_{yi})$, kg/kg
 y = Miscellaneous organics, %
 y_1 = Ist stage temperature, $^{\circ}C$
 y_3 = IIIrd stage temperature, $^{\circ}C$
 y_5 = Vth stage temperature, $^{\circ}C$
 Y_B = Yield on bleaching, %
 Y_{up} = Yield of UP, %,
 Z = Objective function, Rs/t(Chap-4)
 Z = Resins fatty acids %(Chap-5)
 $298K \int^{T_2} =$ Sensible heat above at $25^{\circ}C$

Greek Symbols

θ = Angle of submergence, Radian
 ρ = Density of water, kg/m^3
 η = Viscosity of filtrate, Ns/m^2
 α_0 = constant for a particular cake
 ρ_{BL} = BL density, kg/m^3
 ρ_f = Density of fibers, kg/m^3
 ρ_s = Density of wash water, kg/m^3
 ϵ_t = Total porosity of cake
 ρ_{wl} = WL density, kg/m^3

ρ_{wl} = WL density, kg/m^3

Subscripts(Except as above)

f=Feed, feed concentration

i,j=Input; effect number (j = 1,2,3,.....n)

v=Vapor

0= Basic fixed reference point.(chap-4)

APPENDIX-XII

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