MANUFACTURE OF FURFURAL

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MANUFACTURE OF FURFURAL

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This is to certify that Mr. Kaushal Kumar Jain Roll No. 170610010022, Ms. Manashi Roy Chowdhury Roll No. 170610010023 and Mr. Rupantar Choudhury Roll No. 170610010037 of B.E. 8th Semester have jointly carried out the project entitled "MANUFACTURE OF FURFURAL" under my supervision and submitted the report in partial fulfilment of the requirement for the Degree of Bachelor of Engineering in Chemical Engineering of Assam Science and Technology University, which may be accepted.

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ABSTRACT

Furfural, one of the principal chemical which acts as a starting reagent to produce several high value-added products. It can be produced from a variety of agricultural waste biomass including sugarcane bagasse, corncobs, oat hulls, wheat brans, rice hulls and sawdust containing polysaccharide hemicellulose (pentosan). The main route for furfural production consists of acid hydrolysis of hemicellulose present in biomass to obtain pentose sugar, which undergoes a dehydration reaction to produce furfural. Due to the presence of an aldehyde group and a conjugated system of double bonds, furfural can participate in several reactions, resulting in formation of a wide range of value-added products. It also acts as an intermediate for synthesizing chemical products such as nylons, lubricants, solvents, adhesives, medicines, and plastics. Furfural is an important renewable, non-petroleum based chemical feedstock. Furfuryl alcohol, a derivative of furfural, by reduction process can be used with phenol, acetone, or urea to make solid resins. Such resins are commonly used in making fibre glass, aircraft components and automotive brakes. Furfuryl alcohol is also used in pharmaceuticals, fungicides, and insecticides. Furfural has several applications such as antacids, fertilizers, plastics, inks, fungicides, nematicides, adhesives and flavouring compounds. This piece of work demonstrates a proposed idea of an industrial furfural manufacturing plant. It explores different characteristic properties of furfural and studies different literatures available to suggest a best suited manufacturing process. It also presents the process description, mass balance and energy balance as well as design calculations of a few equipment used in the proposed industrial manufacturing plant. It also spotlights some of the important applications and uses of furfural.

TABLE OF CONTENTS

TABLE OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION AND LITERATURE SURVEY

1.1 INTRODUCTION

Furfural is an organic compound derived from a variety of agricultural byproducts, that includes saw dust, bagasse, corn cubs, etc. Many forms of ligno-cellulosic biomass such as hardwood trees contain raw materials that can be hydrolysed easily to produce pentose sugars such as xylose, arabinose etc. which on further hydrolytic action yields furfural.

It is among the important biobased chemicals in biorefineries. It is a ring-structured heterocyclic aldehyde which is a colorless, oily liquid having odor of almonds which quickly darkens when exposed to air and dissolves readily in most polar organic compound but slightly soluble in either water or alkanes. It is toxic and flammable, and a versatile platform chemical that can be employed to produce green fuel and chemical intermediates. [1]

Table 1.1 Properties of Furfural

Properties	Specification
Chemical Formula	$C_5H_4O_2$
Molar Mass	96.085 $g.mol^{-1}$
Appearance	Colorless Oil
Odor	Almond like
Density	1.1601 $g.ml^{-1}$ (20 °C)
Melting Point	-37 °C (-35 °F; 236 K)
Boiling Point	161.7 °C (324 °F; 435 K)

Solubility in water	83 g/L
Vapor Pressure	2 mm Hg (20°C)
Magnetic susceptibility	-47.1×10^{-6} cm^3/mol

Furfural was first discovered in the year 1821 by a German chemist, Johann Wolfgang Döbereiner, who produced a small sample as a byproduct of formic acid synthesis. It was observed that furfural can be obtained from various vegetable substances. In 1840, Scottish chemist, John Stenhouse assigned the empirical formula for furfural to be $C_5H_4O_2$. In the year 1845, British chemist, George Fownes proposed the name 'furfurol' but was changed to furfural because of presence of aldehyde and the German chemist, Carl Harries deduced the structure of furfural in 1901. [2]

Furfural has two important functional groups, one being an aldehyde and the other being a conjugated system which helps in various applications. It is generally extracted from pentose, more precisely from xylose.

Furfural is an important renewable, non-petroleum based and chemical feedstock. It undergoes hydrogenation to form furfuryl alcohol which is a chemical intermediate used in the mass production of furan resin prepolymers used in thermostat polymer matrix composite, adhesives, casting resins, cement, etc. It is used as a fungicide, weed killer, can be used as a solvent for lubricating oils, to improve the characteristics of diesel fuel etc. [2]

The acceptance of furfural as a substitute for petrochemicals as a basic material for the production of tetrahydrofuran, furfuryl alcohol resins, and as a biofuel. A high oxygen content of furfural as compared to conventional fuel additives improves combustion and reduces smoke emissions in diesel engines and lowering diesel cost. It is formed by dehydrating five carbon sugars such as xylose and arabinose that can be acquired from the hemi-cellulose fraction of lignocellulosic biomass. Various chemical reactions such as Grignard reactions and aldol and Knoevenagel condensation can occur in furfural through the aldehyde functional group.

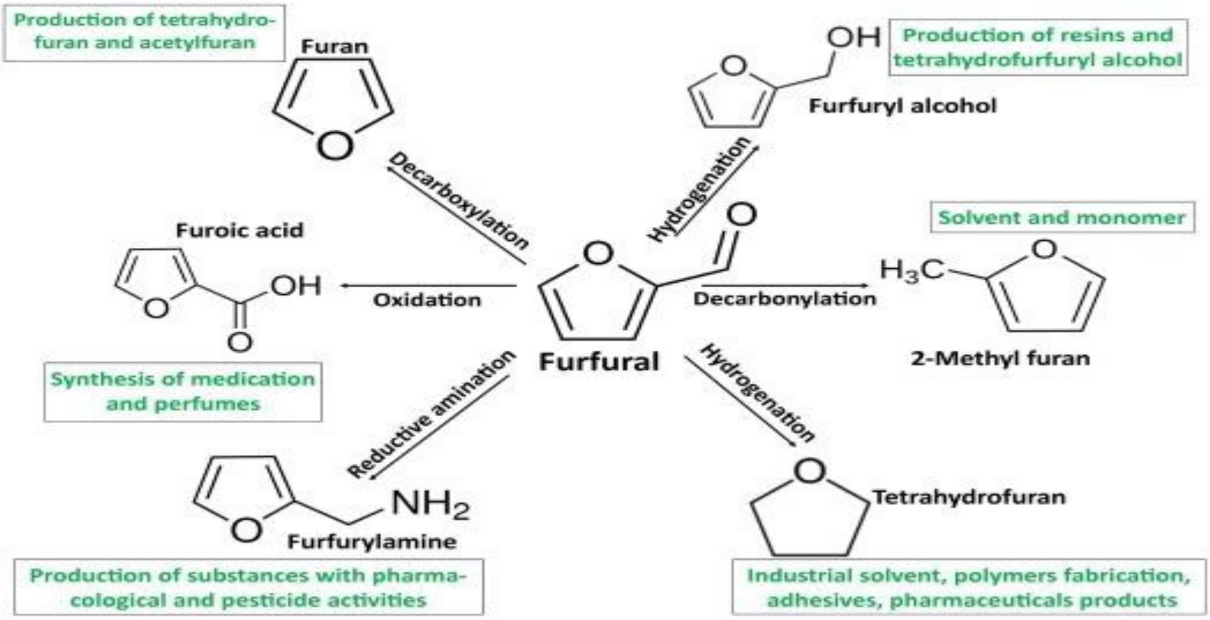

Fig. 1.1 Derivatives of furfural and its application.

Under the economy circle concept, the study of reaction zone in the production of furfural is important because it allows to reduce the excessive use of water, high energy consumption and the formation of decomposition products by reducing the separation costs. Furfural production is exclusively based on the acid-catalyzed conversion of pentosan sugars present in agricultural and forestry residues. [1] [2]

1.1.1 USES OF FURFURAL

Furfural and its derivates has been extensively used in plastics, pharmaceutical and agro-chemical industries. Furfural and its derivatives have been widely used as fungicides and nematicides, transportation fuels, gasoline additives, lubricants, resins, decolorization agents, jet fuel blend stocks, drugs, insecticides, bio-plastics, flavour enhancers for food and drinks, rapid oil weather report systems for bomb damaged runways and potholes and also for food modifications and book preservation. [1] [2]

1.2 LITERATURE SURVEY

Furfural (IUPAC name- 2-furaldehyde) of the fural family, is the source of the other technically important furans. The solubility of furfural is 8.3% at 20 °C and is completely dissolves in alcohol and ether. Its boiling point is 161.7°C. The first commercial production of furfural started in the year 1922. The raw materials used as a feed in the production process are corn cubs, oat hulls, rice husks, bagasse, and saw dust. [2]

1.2.1 VARIOUS INDUSTRIAL PROCESS OF MANUFACTURE OF FURFURAL [1]

(1) Vedernikov developed a single-stage furfural production process based on simultaneous hydrolysis and dehydration of lignocellulosic biomass to furfural in dilute sulphuric acid solution. Because the pentoses formed would spontaneously be converted into furfural, the presence of any other pentoses in the solution would be limited, and so, the occurrence of side reactions and therefore, by-products would be minimal. As such, yield increases marginally (75% in this case). Moreover, biomass cellulose appears to be preserved in this process, which boosts the downstream application of cellulose in the production of other chemicals, such as ethanol. [3]

(2) In the second process, furfural was being manufactured using a novel reactor known as the multi-turbine column (MTC). In this process, the hemi cellulosic pentosans, which is obtained from pre-hydrolysis of straw, is acid hydrolysed first to xylose and simultaneously converted into furfural in one continuous reactor which is a one-step process. In this process, 5 wt.% aqueous solution which contains pentosans was used as feed, which was directly added to the column. Furfural was produced in aqueous phase in the reactor and was transferred into vapour phase. Various additives, such as acids and salts were used to improve yield, and it was observed that the concentration of acid (HCl or H_2SO_4) and NaCl affected furfural production. The yield was 83% and the purity was over 99% were obtained under optimal conditions of

0.18 wt.% HCl, 1.7 M NaCl at 200°C. This method had an advantage of minimal formation of by-products such as HMF, acetic acid, and formic acid. As the process is continuous, it features low energy consumption, and therefore seems to be a more appropriate alternative to the conventional batch process. However, the optimal yield is achieved only when dilute solutions (5 wt.%) of pentosans are used. And so, lignocellulosic biomass cannot be directly used in this process. [3]

1.2.2 VARIOUS LABORATORY PROCESS OF MANUFACTURE OF FURFURAL [1]

(1) Furfural production in autocatalytic systems:

Biomass is treated at high temperature (200 °C or higher) and pressure in batch systems to produce furfural. In this process, acetic acid is released from hydrolysis of acetyl groups present in the biomass hemicelluloses and acts as a catalyses the reaction. The hemicelluloses are isolated from biomass, depolymerized to pentoses and hexoses, and concurrently the pentoses and hexoses are converted to furfural and HMF respectively. [3]

(2) Furfural production in aqueous-acid catalytic systems:

The batch production process was studied using commercial xylose solutions (0.067–0.20 mol/L) as a feedstock and formic acid as the catalyst under different experimental conditions. The xylose conversion rate was increased from 6.2% to 98.2% by increasing temperature from 120 °C to 200 °C was observed. The furfural yield was increased (from 3.0% to 65.4%) by increasing temperature (from 140°C to 200 °C), whereas it decreased with increasing time (from 20 min to 40 min). The selectivity of furfural production varied from 42.3% to 72.7% under different conditions. [3]

(3) Furfural production in bi-phasic systems:

In this method, furfural is produced from pentose (mainly xylose) in an aqueous phase, and the formed furfural will spontaneously be transferred from the aqueous phase to organic phase in which the furfural is extracted from the batch. The reaction medium (aqueous phase) containing acid catalysts has a limited concentration of furfural as the furfural is instantaneously transferred as it is formed, which improves the overall yield. The objective of a bi-phasic reaction is to reduce side reactions and to avoid the azeotropic point of the furfural-water mixture, which makes separation difficult.

Furfural and its derivatives have been extensively used in plastics, pharmaceutical and agrochemical industries. Furfural and its derivatives have been widely used as fungicides and nematicides, transportation fuels, gasoline additives, lubricants, resins, decolorizing agents, jet fuel blend stocks, drugs, insecticides, bioplastics, flavor enhancers for food and drinks, rapid all weather report systems for bomb damaged runways and potholes and also for food modification and book preservation. [3]

1.2.3 ACID-CATALYZED HYDROLYSIS OF RICE HULL [2]

Furfural production was accomplished initially with the pre-hydrolysis of 10 gm sample in 100 ml of 3% $\frac{wt}{wt}$ sulfuric acid at different reflux times. After this step, the hydrolyzed product was regulated to 250 ml in 50% sulfuric acid and heated with the help of an electric mantle. During the heating process, furfural was produced by steam distillation. The catalysts, $AlCl_3$, $ZnCl_2$, ZnO and TiO_2 were obtained commercially and used without any further purification. Zirconium oxide was made by impregnation of alumina with zirconyl chloride and then heated in an oven at 700 °C for an hour. TiO_2 was prepared by percolation of commercial TiO_2 with 1 N H_2SO_4 heated at 700 °C for an hour. When the experiments were carried out on whole rice hulls using the optimal conditions of 15% H_2SO_4, L/S 25 ml/gm, 30 minutes, the yield was about was decreased.

The catalyst used in the reaction acts as Lewis acid and stabilize intermediates in the dehydrocyclization of pentoses. Aluminium chloride appears to be the strongest Lewis acid, but titanium dioxide improves the yield of furfural production. It is further carried out in two different mechanism. [4]

1.2.3.1 FURFURAL PRODUCTION IN TWO-STAGE PROCESS

In this two-stage process, initially pentoses are separated from lignocellulosic substances in a pre-hydrolysis step. In the second step, dehydration of the sugar molecules takes place. The process was performed in 3% H_2SO_4 with the sample at different times. A sample without pre-hydrolysis results in low efficiency in yield step. To achieve higher yield, the pre-hydrolysis process is carried put for 30 minutes.

1.2.3.2 FURFURAL PRODUCTION IN ONE-STAGE PROCESS

In the one-stage process, samples were autoclaved under mild condition to break down the sugar molecules from the lignocellulosic substances. When the reaction takes place in the autoclave, the yield goes up to 3.34 % dry basis at 20 % $\frac{wt}{wt}$ sulfuric acid. This yield is low as compared to the yield of furfural produced from corn cubs. [5]

1.2.4 DILUTE ACID HYDROLYSIS OF LIGNOCELLULOSICS

The production of furfural by dilute acid hydrolysis of lignocellulosic materials gives a yield of about 40 – 60 % of the theoretical value in closed systems and it changes to 50 – 80 % when it is rapidly removed from reaction medium. The yield calculations are simple in this system because the amount of biomass used in the feedstock is of known quantity. But, when continuous units are used, the calculations become difficult because the mass flow rate fed to the reactor is unknown. The operating conditions in the tubular reactor were 6 – 6.6 % slurry consistency, 0.6 % H_2SO_4 concentration, 200 – 230 °C and residence time is about 95 – 105 seconds. Depending on the operating conditions, reaction temperature and residence time can vary. Reactors used in this process were either autoclaves or continuous reactors. In some special cases, a co-catalyst can also be used (example, sea salt). If high yield is to be achieved, the furfural formed should be separate from the acidic medium. Furfural yield is commonly expressed as a percent of the theoretical value. Therefore, it is important to know the exact quantity of wood introduced into the reactor to get the precise results.

The quantitative analysis of the product formed can be done by high performance liquid chromatography (HPLC) and gas chromatography (GC). [5]

CHAPTER 2

PROCESS SELECTION

During the literature survey, we have come across various processes used in the production of Furfural. In order to choose a particular process for furfural production, the following table gives a comparison between the processes based on reaction conditions such as optimum temperature, residence time, yield of the process and purity of the product obtained. [5]

Table 2.1 Comparison of various production processes of Furfural

Sl No	Raw Material	Catalyst	Temperature	Time	Reactor	Yield (%)	Reference
1.	Xylose	H_2SO_4,1N	300°C	1-2 sec	PFR	60-70	Medeiros and Burnet 1983
		H_2SO_4+ NaCl	230-250°C	5-6 min	Batch	75-83	Chunguang Rong et. al. 2011
2.	Rice Husk	H_2SO_4, 1.6%	180°C	2 h	Autoclave	38-49	Ren Suxia et. Al. 2012
		H_2SO_4, 0.5M	185°C	2 h	Autoclave	50	Sharma and Sahgal 1982
3.	Bagasse	H_2SO_4, 1:3 ratio with feed	170-185°C	3 h	Batch	45-50	Leyanis Mesa et al. 2014
		H_2SO_4, 1%	110°C	90 min	Batch	20-34	S. K. Uppal et. Al. 2008
4.	Hardwood	H_2SO_4 + NaOH	200-230°C	2 min	Tubular PFR	40-60	F. Carrasco 1992
		H_2SO_4, 0.8%	200-230°C	2 min	PFR	40-55	Abatzoglou et al. 1990

From the above comparison table, we can conclude that Furfural production from xylose is economically not viable for industrial use due to its cost factor even though the reaction conditions are highly favorable. Again, with the raw material as bagasse, the reaction time is very high with lower yield that result in its less viability, thus more options can be explored. With rice husk as the feed, high reaction time is a big concern. But when hardwood is used as the raw material, the reaction conditions are better, with relatively cheaper raw material makes it the most viable option. But since hardwood is not feasible due to its availability and other environmental factors, with the same process and same reaction conditions, the raw material is changed to biomass which is a combination of hardwood, bagasse, and rice husk. [5]

CHAPTER 3

PROCESS DESCRIPTION

3.1 PRODUCTION PROCESS OF FURFURAL BY DILUTE ACID HYDROLYSIS OF LIGNOCELLULOSES

The acid catalysed hydrolysis of the pentosans and hexosans present in lignocellulose is a heterogeneous reaction where the reactants are in the solid phase and the catalyst in the aqueous phase.

3.1.1 RAW MATERIALS USED:

The raw material used in this process is a mixture of hardwood, bagasse, rice husk. The mixture was ground and screened up to a mesh size of 0.25mm. Grinding is done as it enhances the accessibility to the lignocellulosic complex and the glycosidic bonds become more accessible to hydrolytic action.

3.1.2 PROCESS DEVELOPMENT UNIT (PDU)

The acid hydrolysis was performed in a Process Development Unit which comprises of the following components-

3.1.2.1 FEED VESSEL

A known quantity of biomass is introduced into the feed vessel to complete a proper mass balance with 5% moisture content. Water is being added to the mixture to accomplish a proper uniformity throughout the mixture. [5]

3.1.2.2 STEAM INJECTOR

The slurry is subjected to direct heating with live steam with the help of an electric boiler. However, steam dilutes the slurry mixture from 9.4% to 6.0- 6.6%. The steam flow rate is necessary to achieve mass balance calculations as well as to calculate the slurry concentration at the starting of the hydrolytic treatment. [5]

3.1.2.3 SHEAR VALVE

The heated slurry from the steam injector is then rapidly pumped at high pressure of about 18-20 MPa with the help of a slurry piston pump. The slurry is then discharged through a homogenizing value to a moderate pressure of 3.5 MPa. [5]

3.1.2.4 ACID INJECTION SYSTEM

Sulphuric Acid (9-10) % $^{\mathrm{wt}}/_{\mathrm{wt}}$ is added via pump to catalyse the reaction at a flowrate of 40ml/min without being consumed in the reaction. [5]

3.1.2.5 TUBULAR REACTOR

The reactor made up of stainless-steel coil of inner diameter 1 cm, thickness of 1.1 mm, length 17.2m. Residence time varies from (98-104) sec with a temperature of (200-230) °C. In the reactor, acid hydrolysis takes place which results in solubilization of the biomass and dehydration reaction occurs that finally leads to the formation of furfural. [5]

Reaction involved:

$$(C_5H_{804})_n \longrightarrow n\ C_5H_4O_2 + 2n\ H_2O$$

3.1.2.6 BASE INJECTION SYSTEM

An aqueous sodium hydroxide solution (8% $^{wt}/_{wt}$) is pumped to neutralize the acid catalyst and to instantaneously conclude the hydrolytic reaction. [5]

Reaction involved:

$$2\ NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ H_2O$$

3.1.2.7 EXPANSION VESSEL

The slurry is then introduced in an expansion vessel at atmospheric pressure which results in flash vaporization which helps to cool down the slurry and separate the volatile products. Apart from water, the condensate includes acetic acid, formic acid, methanol, ethanol, HMF which wholly named as cellulose dehydrating product (CDP). [5]

3.1.2.8 DISTILLATION COLUMN

Finally, from the expansion vessel, the products enter the atmospheric distillation column where the components are separated into distillate and bottom product. The distillate contains maximum amount of water and CDP and less amount of furfural whereas the bottom product comprises maximum amount of furfural in it and less amount of CDP and water. If the purity of furfural in the bottom product is above the required value, it is then passed to a storage tank where it can be stored before it gets transferred to the bottling unit. [5]

CHAPTER 4

FLOWCHART

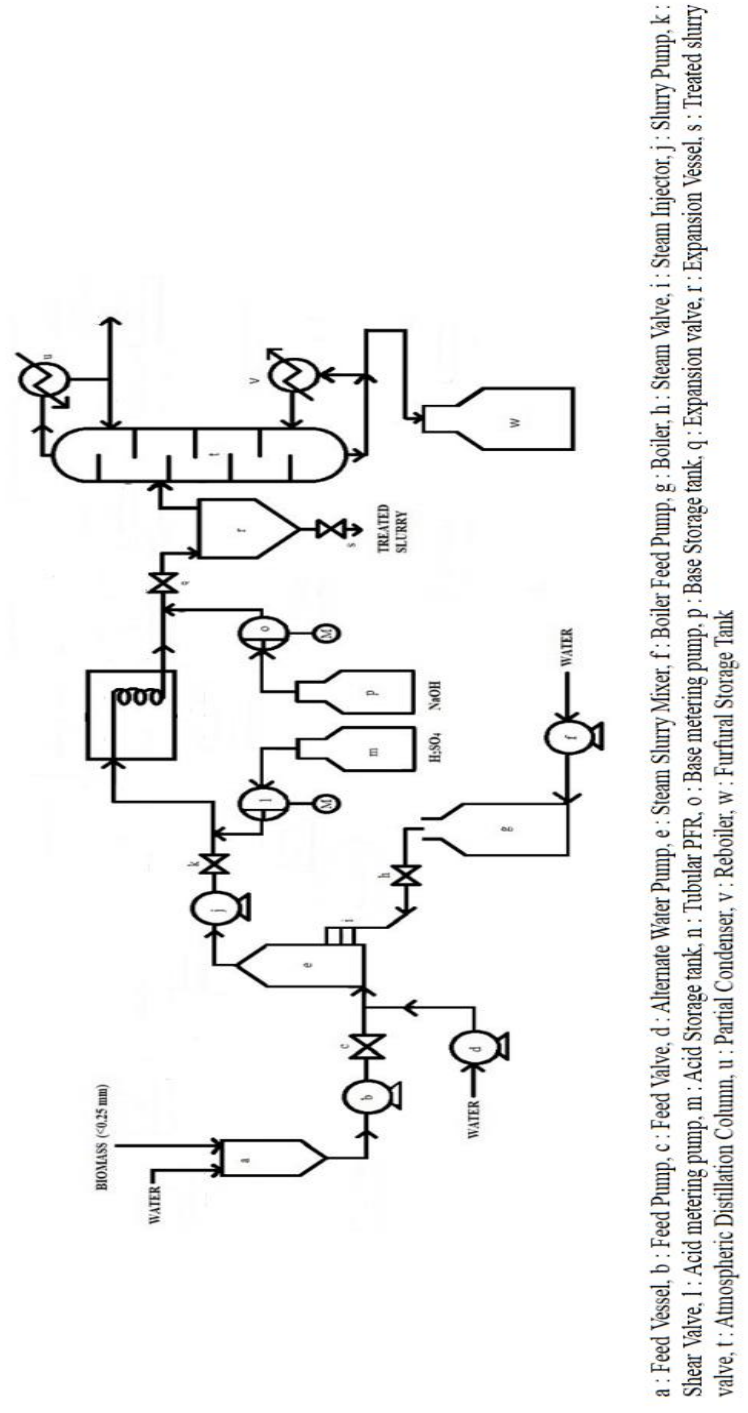

Fig 4.1: Flowchart of furfural production.

CHAPTER 5

MATERIAL BALANCE

OVERALL ASSUMPTIONS:

1. There is no loss.
2. There is no accumulation of mass.
3. Conversion is 90%.
4. Conversion of 98% of furfural from liquid to vapor in expansion vessel.
5. Separation of 95% of furfural in distillation column.

Basis: 100 kg/hour of biomass and one hour operation.

DATA:

Specific Heat Values:

1. The specific heat value for cellulose is, $C_{P_{Cellulose}}$ = 1.3388 KJ/kg-K [6]
2. The specific heat value for hemicellulose is, $C_{P_{Hemicellulose}}$ = 1.4 KJ/kg-K [7]
3. The specific heat value for lignin with impurities is, $C_{P_{Lignin}}$ = 1.10 KJ/ kg-K [8]
4. The specific heat value for water is, $C_{P_{Water}}$ = 4.1785 KJ/ kg-K [9]
5. The specific heat value of steam, $C_{P_{Steam}}$ = 1.9892 KJ/kg-K [10]

Latent heat of Vaporization:

1. Latent Heat of Vaporization for Water, λ^{H_2O} = 2250 KJ/kg [11]

For steam at 250 °C:

1. H = 1164 btu/lb [12]
2. h = 218.59 btu/lb [12]
3. λ = (1164 – 218.59) = 945.41btu/lb = $\frac{945.41}{0.45}$ btu/kg

Feed composition:

Feed for the process is a biomass consisting of hardwood, bagasse, and rice husks. The percentage of the items in the feed are assumed considering availability and reaction parameters from the comparison table. Moisture content of maximum 5% of the total weight of biomass is allowed.

Table 5.1 Biomass composition

Feed Composition	**Percentage**	**Weight (kg)**
Hardwood	35	33.25
Bagasse	40	38
Rice Husk	25	23.75
Moisture	5	5

Table 5.2 Chemical composition of biomass constituents

Content (kg)	**Cellulose**		**Hemicellulose**		**Lignin & Others**	
	Percentage	**Weight (kg)**	**Percentage**	**Weight (kg)**	**Percentage**	**Weight (kg)**
Hardwood	45	14.9625	30	9.975	25	8.3125
Bagasse	39	14.82	37	14.06	24	9.12

Rice Husk	35	8.3125	25	5.9375	40	9.5

Table 5.3 Chemical composition of feed in 100 kg biomass

Cellulose	38.095
Hemicellulose	29.9725
Lignin & others	26.9325
Water	5

5.1 STAGE 1: FEED VESSEL

The feed vessel is fed with the raw materials which is a mixture of biomass (cellulose, hemicellulose, lignin, and others) which is stream A and with water (B) to reduce the viscosity.

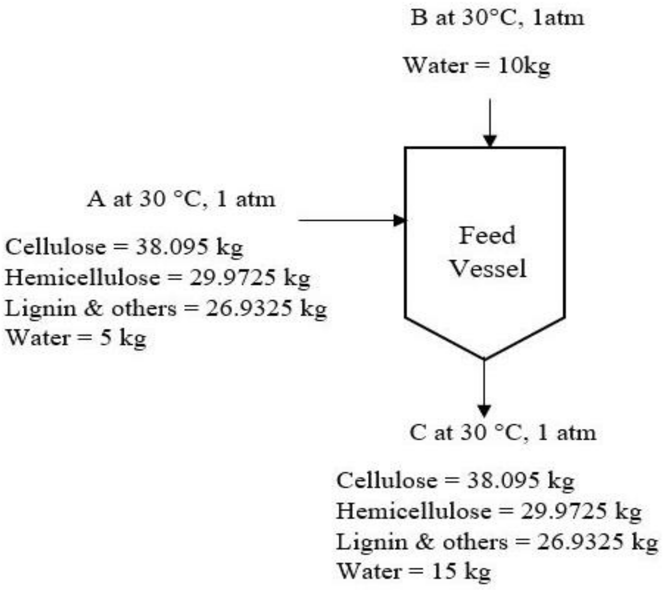

Fig. 5.1 Material balance over feed vessel.

<u>Mass In</u>:

Amount = $M_A + M_B$

= (38.095 + 29.9725 + 26.9325 + 5) + 10

= 110 kg

Mass Out:

Amount = M_C

= (38.095 + 29.9725 + 26.9325 + 15)

= 110 kg

Table 5.4 Material balance over the feed vessel

Materials	Input				Output	
	A		B		C	
	Amount (kg)	**Amount (kmol)**	**Amount (kg)**	**Amount (kmol)**	**Amount (kg)**	**Amount (kmol)**
Cellulose	38.095	0.235	-	-	38.095	0.235
Hemicellulose	29.9725	0.173	-	-	29.9725	0.173
Lignin and Others	26.9325	0.0178	-	-	26.9325	0.0178
Water	5	0.278	10	0.555	15	0.833
Total	100		10		110	
Total Input = 110 kg					Total Output = 110 kg	

5.2 STAGE 2: STEAM-SLURRY MIXTURE

The output (C) from the feed vessel is sent to a steam-slurry mixture where steam (D) is injected.

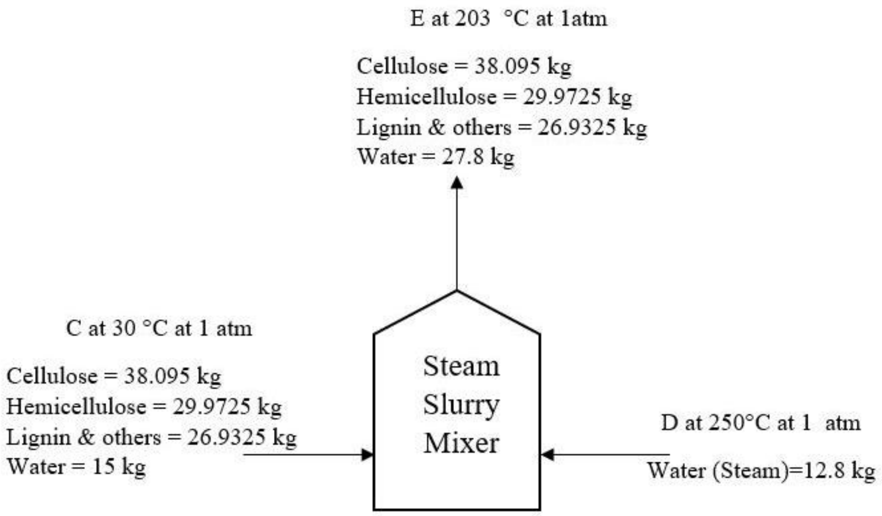

Fig. 5.2 Material Balance over the steam-slurry mixture.

As the quantity of steam rejected is unknown, we can calculate the required amount from energy balance equation. Let the amount of steam required be x kg and w_C , w_H , w_L , w_W be the weight fraction of cellulose, hemicellulose, lignin, and water respectively.

$$w_C = \frac{38.095}{110} = 0.346$$

$$w_H = \frac{29.9725}{110} = 0.272$$

$$w_L = \frac{26.9325}{110} = 0.246$$

$$w_W = \frac{15}{110} = 0.136$$

$$C_{P_{Avg}} = \Sigma w_i C_{p_i}$$

$$= (0.346 \times 1.3388) + (0.272 \times 1.4) + (0.246 \times 1.1) + (0.136 \times 4.1725)$$

$$= 1.68208 \text{ KJ/Kg-°C}$$

$$C_{P_{out}} = (\frac{38.095}{110+x} \times 1.3388) + (\frac{29.9725}{110+x} \times 1.4) + (\frac{26.9325}{110+x} \times 1.1) + (\frac{15+x}{110+x} \times 3.305)$$

By energy balance equation,

⇨ $[110 \times 1.68208 \times (30\text{-}25)] + x\,[(4.1725 \times (100\text{-}75)) + 2250 + (1.98 \times (250\text{-}100))] = (110+ x) \times C_{P_{out}} \times (200\text{-}25).$

⇨ $925.144 + 2859.9375\ x = (110+ x) \times [(\frac{51.002}{110+x} + \frac{41.9615}{110+x} + \frac{29.6257}{110+\mathrm{x}} + \frac{3.303(15+x)}{110+x})] \times (200-25)$

⇨ $925.144 + 2859.9375\,x = 175\,(172.1642+3.305\,x)$

⇨ $x = 12.8$ kg

<u>Mass In</u>:

Amount = $M_C + M_D$

= (38.095+29.9725+26.9325+15) + 12.8

= 122.8 kg

<u>Mass Out</u>:

Amount = M_D

= (38.095+29.9725+26.9325+27.8)

= 122.8 kg

Table 5.5 Material balance over steam-slurry mixture

Materials	**Input**				**Output**	
	C		**D**		**E**	
	Amount (kg)	**Amount (kmol)**	**Amount (kg)**	**Amount (kmol)**	**Amount (kg)**	**Amount (kmol)**
Cellulose	38.095	0.235	-	-	38.095	0.235
Hemicellulose	29.9725	0.173	-	-	29.9725	0.173

Lignin and Others	26.9325	0.0178	-	-	26.9325	0.0178
Water	15	0.833	12.8(Steam)	0.711	27.8	1.544
Total	110		12.8		122.8	
Total Input = 122.8 kg					Total Output = 122.8 kg	

5.3 STAGE 3: ADDITION OF H_2SO_4

The output (E) from steam-slurry mixture is mixed with small amount of H_2SO_4 (F) to act as a catalyst, and the mixture (G) contains a mixture of cellulose, hemicellulose, lignin with other impurities, water, and H_2SO_4.

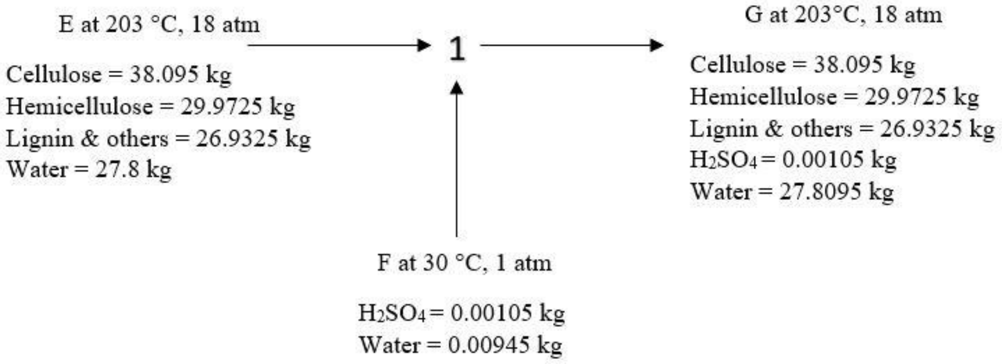

Fig. 5.3 Material Balance due to addition of H_2SO_4

Calculations:

Flow rate of H_2SO_4 = 40 ml/min

$$= \frac{40\times 60}{1000} \text{ l/hr}$$

$$= \frac{2.4}{22.4} \times \frac{98}{1000}$$

= 0.0105 kg

Concentration of H_2SO_4 = 10 % $^{wt}/_{wt}$ [5]

Amount of H_2SO_4 added = $\frac{10}{100} \times 0.0105 = 0.00105$ kg

Amount of H_2O = 0.00945 kg

<u>Mass In</u>:

Amount = $M_E + M_F$

= (38.095+ 29.9725+26.9325+27.8) + (0.00945+0.00105)

= 122.8105 kg

Amount = M_G

= (38.095+ 29.9725+26.9325+ 27.8095+ 0.00105)

= 122.8105 kg

Table 5.6 Material balance due to addition of H_2SO_4

Materials	**Input**				**Output**	
	E		**F**		**G**	
	Amount (kg)	**Amount (kmol)**	**Amount (kg)**	**Amount (kmol)**	**Amount (kg)**	**Amount (kmol)**
Cellulose	38.095	0.235	-	-	38.095	0.235
Hemicellulose	29.9725	0.173	-	-	29.9725	0.173
Lignin and Others	26.9325	0.0178	-	-	26.9325	0.0178
Water	27.8	1.544	0.00945	0.000524	27.8095	1.545
Sulphuric Acid			0.00105	0.000011	0.00105	0.000011
Total	122.8		0.0105		122.8105	
Total Input = 122.8105 kg					Total Output =122.8105 kg	

5.4 STAGE 4: PFR REACTOR

The stream G is now allowed to enter the reactor where reactions take place as

$$(C_5H_80_4)_n \xrightarrow{\hspace{2cm}} n\,C_5H_4O_2 + 2n\,H_2O$$

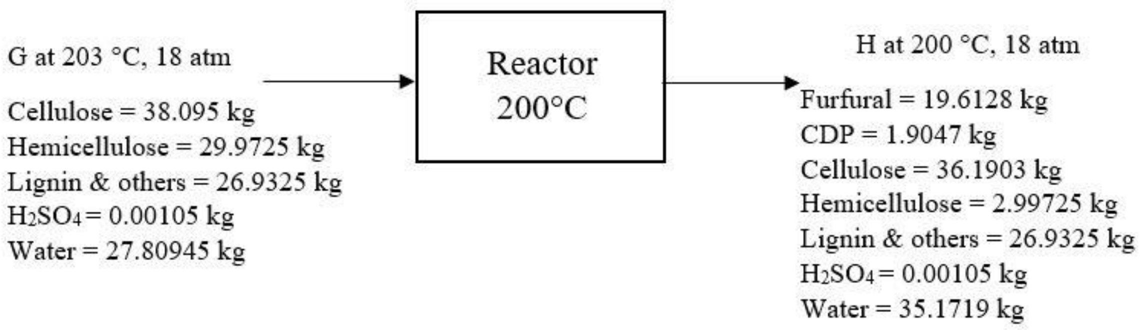

Fig. 5.4 Material balance over PFR

As the efficiency is 90%, we proceed the further reaction. Although it is known that cellulose is more complex than hemicellulose, but under this condition, it will also undergo dehydration; assuming the conversion to b 5% (cellulose). The major constituents of CDP (cellulose dehydration product) are methanol, ethanol, formic acid, and acetic acid.

$$(C_5H_80_4)_n \xrightarrow{\hspace{2cm}} n\,C_5H_4O_2 + 2n\,H_2O$$

The molecular mass of hemicellulose is 132 kg/kmol.

Molecular mass of furfural = 96 kg/kmol

Molecular mass of water = 18 kg/kmol

Total hemicellulose present = 29.9725 kg = $^{29.9725}/_{132}$ = 0.2273 kmol

Number of moles of hemicellulose reacting = 0.2043 kmol [90% conversion]

Number of moles of unreacted hemicellulose = 0.023 kmol

1 mole of hemicellulose gives 1 mole of furfural and 2 moles of water.

∴ 0.2043 kmol of hemicellulose gives 0.2043 kmol of furfural and 0.4086 kmol of water with 0.023 kmol of hemicellulose unreacted.

The reaction for cellulose is given as

$C_6H_{10}O_5 \xrightarrow{\hspace{3em}}$ Cellulose Dehydration Product (CDP)

Total cellulose present = 38.095 kg

Total CDP present = 38.095 × 0.05 = 1.9047 kg [5% conversion]

Total unreacted cellulose = 36.1903 kg

Table 5.7 Material balance over reactor

Materials	**Input**		**Output**	
	G		**H**	
	Amount (kg)	**Amount (kmol)**	**Amount (kg)**	**Amount (kmol)**
Cellulose	38.095	0.235	36.1903	0.223
Hemicellulose	29.9725	0.173	2.99725	0.017
Lignin and Others	26.9325	0.0178	26.9325	0.0178
Water	27.80945	1.545	35.1719	1.954
Sulphuric Acid	0.00105	0.000011	0.00105	0.000011
Furfural	-	-	19.6128	0.204
CDP	-	-	1.9047	0.041
Total	122.8105		122.8105	
Total Input = 122.8105 kg			Total Output =122.8105 kg	

5.5 STAGE 5: ADDITION OF NaOH

As the reaction is completed, the output stream H is now fed with a small amount of NaOH to neutralize the extra H_2SO_4 present to stop further conversion.

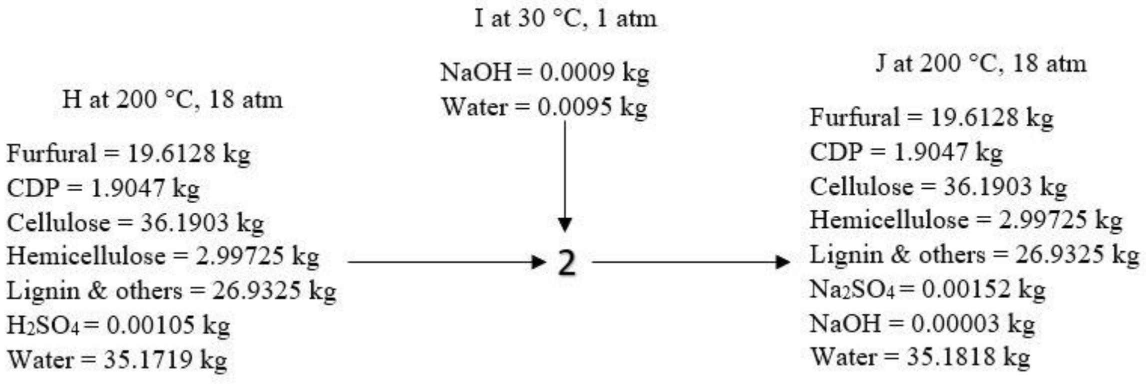

Fig. 5.5 Material balance due to addition of NaOH

$$2\ NaOH + H_2SO_4 \xrightarrow{\qquad\qquad} Na_2SO_4 + 2\ H_2O$$

For 1 mole of H_2SO_4, 2 moles of NaOH are required.

For 0.000011 kmol H_2SO_4, 0.000022 kmol of NaOH is required.

And for 0.000022 kmol of NaOH used, 0.000011 kmol of Na_2SO_4 and 0.000022 kmol of H_2O is formed.

Therefore, weight of NaOH used = 8.8×10^{-4} kg

Concentration of NaOH = 9 % $^{wt}/_{wt}$ [5]

So, the amount of NaOH in the solution = $\frac{9}{109} \times x$

Where, x = weight of NaOH solution

$$8.8 \times 10^{-4} = \frac{9}{109} \times x$$

$$x = 0.01039 \text{ kg}$$

Also, $0.01039 = \frac{y}{22.4} \times \frac{40}{1000}$

Where, y = flow rate of NaOH in liter/hour

$$y = \frac{0.01309 \times 22.4 \times 1000}{40}$$

$$y = 5.82 \text{ liter/hour} = \frac{5.82 \times 60}{1000} = 97 \text{ ml/min}$$

Table 5.8 Material balance while adding NaOH

Material	Input				Output	
	H		I		J	
	Amount (kg)	Amount (kmol)	Amount (kg)	Amount (kmol)	Amount (kg)	Amount (kmol)
Furfural	19.6128	0.204	-	-	19.6128	0.204
Water	35.1719	1.954	0.0095	0.00053	35.1818	1.9545
CDP	1.9047	0.041	-	-	1.9047	0.041
Cellulose	36.1903	0.223	-	-	36.1903	0.223
Hemicellulose	2.99725	0.017	-	-	2.99725	0.017
Lignin & others	26.9325	0.018	-	-	26.9325	0.018
Na_2SO_4	-	-	-	-	0.00152	0.00001
NaOH	-	-	0.0009	0.000021	0.00003	0.0000007
H_2SO_4	0.00105	0.000011	-	-	-	-
Total	122.8105	-	0.0104	-	122.8209	-
Total Input = 122.8209			Total = 122.8209			

5.6 STAGE 6: EXPANSION VESSEL

After neutralization of H_2SO_4, the stream J consists of both volatile (furfural, CDP) and non-volatile (NaOH, Na_2SO_4) components which is separated using an expansion vessel.

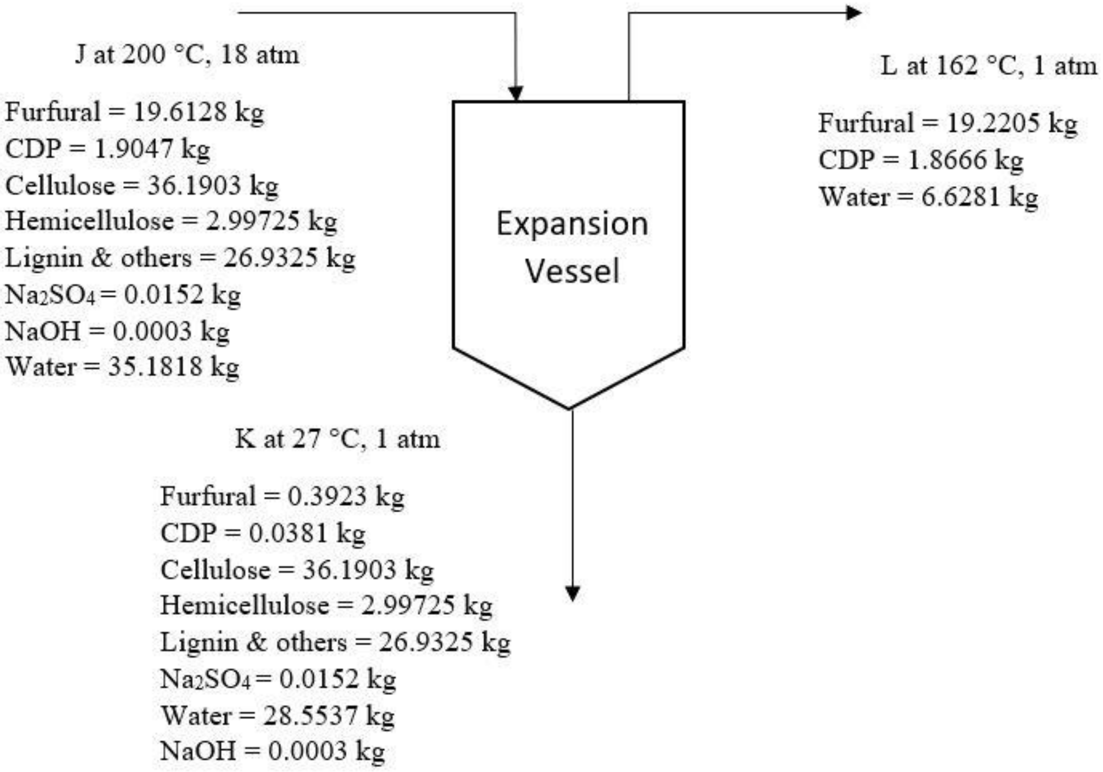

Fig. 5.6 Material balance over expansion vessel

After separation, the stream K is discarded, and the output stream L is sent for distillation for further separation.

Assuming 98% of furfural gets vaporized,

<u>Amount in</u>:

$m_{\text{Furfural}} = 19.6128$ kg

$m_{\text{CDP}} = 1.9047$ kg

<u>Amount out</u>:

For furfural,

$m_{\text{Furfural}} = m_{\text{Furfural}_K} + m_{\text{Furfural}_L}$

$m_{\text{Furfural}} = (0.02 \times 19.6128) + (0.98 \times 19.6128)$

$m_{Furfural}$ = 19.6128 kg

For CDP,

$m_{CDP} = m_{CDP_K} + m_{CDP_L}$

$m_{CDP} = (0.02 \times 1.9047) + (0.98 \times 1.9047)$

m_{CDP} = 1.9047 kg

Table 5.9 Material balance over expansion vessel

Material	Input		Output			
	J		K		L	
	Amount (kg)	Amount (kmol)	Amount (kg)	Amount (kmol)	Amount (kg)	Amount (kmol)
Furfural	19.6128	0.204	0.3923	0.004	19.2205	0.200
Water	35.1818	1.9545	28.5537	0.039	6.6281	0.3682
CDP	1.9047	0.041	0.0381	0.001	1.8666	0.040
Cellulose	36.1903	0.223	36.1903	0.223	-	-
Hemicellulose	2.99725	0.017	2.99725	0.017	-	-
Lignin & others	26.9325	0.018	26.9325	0.018	-	-
Na_2SO_4	0.00152	0.00001	0.00152	0.00001	-	-
NaOH	0.00003	0.0000007	0.00003	0.0000007	-	-
Total	122.8209	-	95.1057	-	27.7152	-
Total Input = 122.8209			Total = 122.8209			

5.7 STAGE 7: DISTILLATION COLUMN

The output stream (L) from the expansion vessel now enters a distillation column where the final separation takes place.

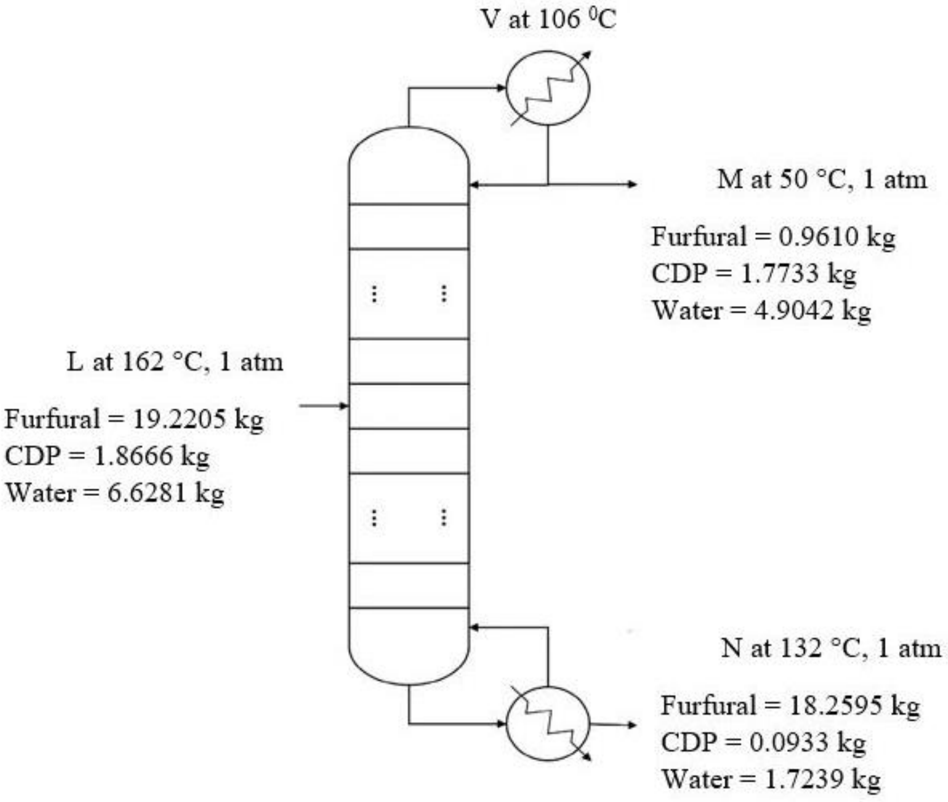

Fig. 5.7 Material balance over distillation column

Assuming 95% of the furfural gets separated.

Amount of furfural in stream N is 95% of furfural from stream L.

For stream N,

$m_{Furfural} = 0.95 \times 19.2205$

$m_{Furfural} = 18.2595$ kg

Table 5.10 Material balance over distillation column

Material	Input		Output			
	L		M		N	
	Amount (kg)	Amount (kmol)	Amount (kg)	Amount (kmol)	Amount (kg)	Amount (kmol)
Furfural	19.2205	0.200	0.9610	0.010	18.2595	0.190

Water	6.6281	0.3682	4.9042	0.2725	1.7239	0.0958
CDP	1.8666	0.040	1.7733	0.038	0.0933	0.002
Total	27.7152	-	7.6385	-	20.0767	-
Total Input = 27.7152kg			Total Output = 27.7152kg			

$$\%\text{purity} = \frac{\text{weight of furfural}}{\text{total weight of bottom product}} \times 100\%$$

$$\%\text{purity} = \frac{18.2595}{20.0767} \times 100\%$$

%purity = 90.94 %

5.8 OVERALL MATERIAL BALANCE

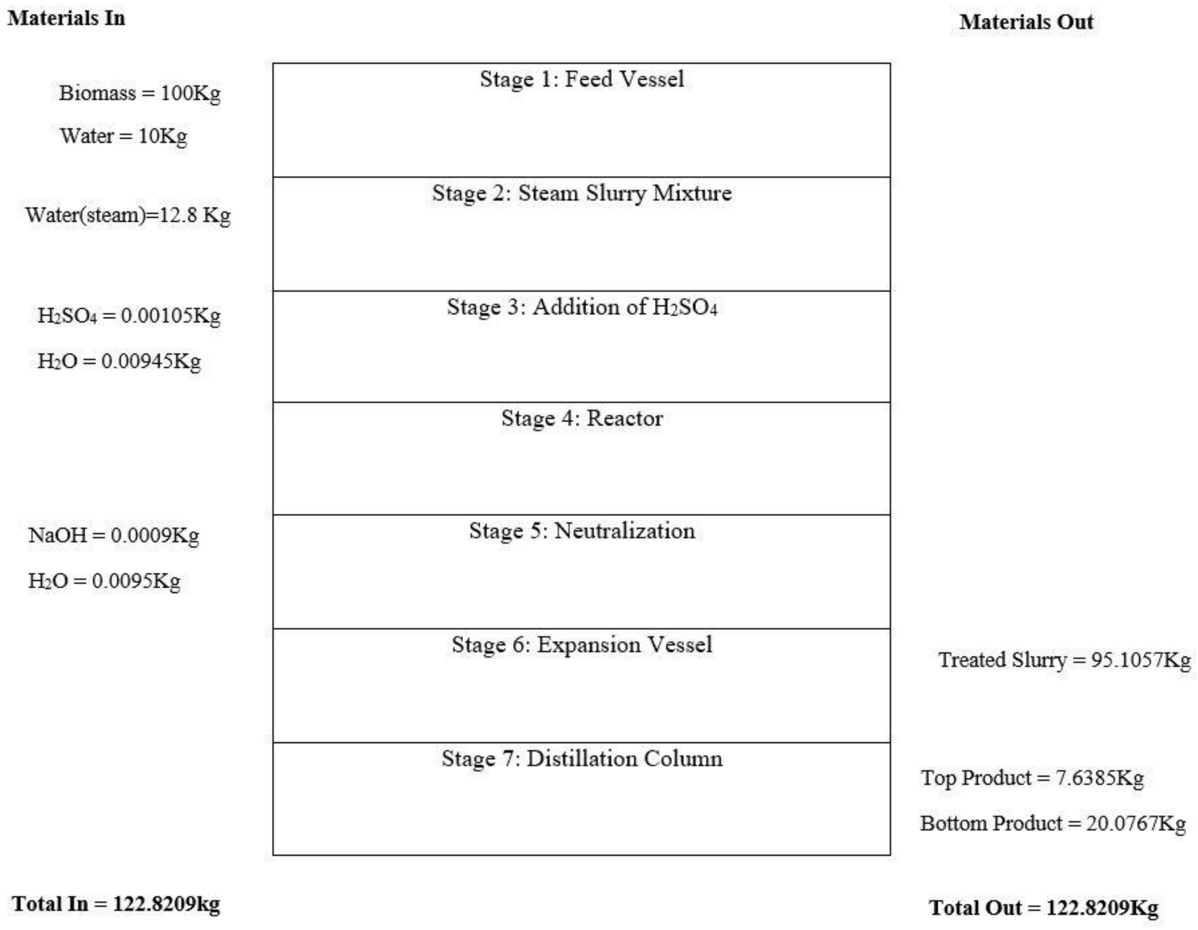

Fig 5.8 Overall material balance.

5.9 MATERIAL BALANCE FLOWCHART

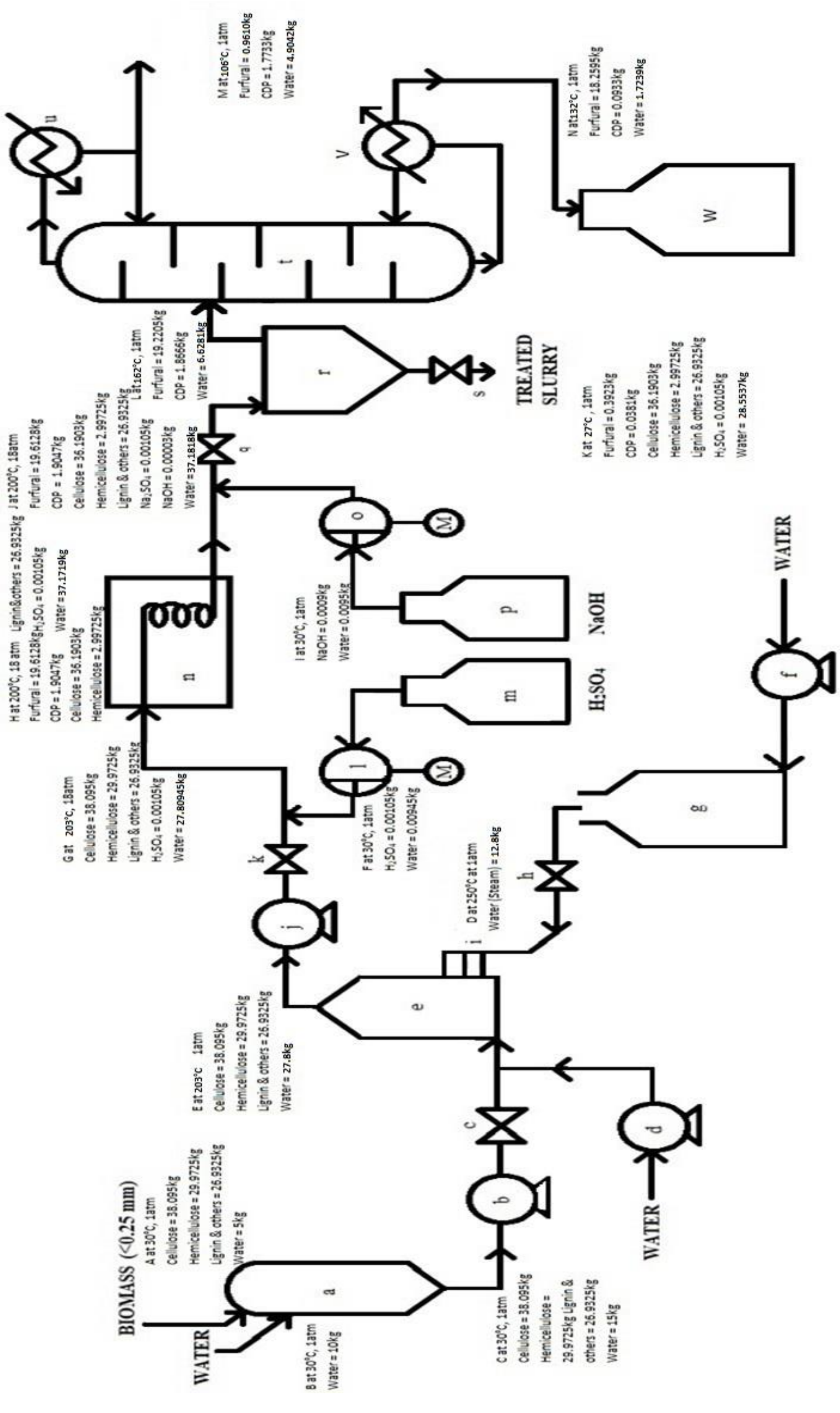

Fig 5.9 Material Balance Flowchart.

CHAPTER 6

MODIFIED MATERIAL BALANCE

Modified Material Balance Calculation:

- Industrial capacity of furfural production plant is 2,000 TPA
- Assuming 330 working days in a year, amount of product from above plant

$$= 20.0767 \text{ x } 24 \text{ x } 330 = 159007.464 \text{ kg/year}$$

- Multiplying factor = (2,000 x 1000)/159007.464 = 12.578 kg/year

6.1 STAGE 1: FEED VESSEL

Table 6.1 Modified Material balance over the feed vessel

Materials	**Input**		**Output**
	A	**B**	**C**
	Amount (kg)	**Amount (kg)**	**Amount (kg)**
Cellulose	479.1589	-	479.1589
Hemicellulose	376.9441	-	376.9441
Lignin and Others	338.7570	-	338.7570
Water	62.8900	125.7800	188.6700
Total	1257.8000	125.7800	1383.58
Total Input = 1383.58			Total Output = 1383.58

6.2 STAGE 2: STEAM SLURRY MIXTURE

Table 6.2 Modified Material balance over the steam slurry mixture

Materials	**Input**		**Output**
	C	**D**	**E**
	Amount (kg)	**Amount (kg)**	**Amount (kg)**
Cellulose	479.1589	-	479.1589
Hemicellulose	376.9441	-	376.9441
Lignin and Others	338.7570	-	338.7570
Water	188.6700	160.9984 (steam)	349.6684
Total	1383.58	160.9984	1544.5784
Total Input = 1544.5784			Total Output = 1544.5784

6.3 STAGE 3: ADDITION OF H_2SO_4

Table 6.3 Modified Material balance due to the addition of H_2SO_4

Materials	**Input**		**Output**
	E	**F**	**G**
	Amount (kg)	**Amount (kg)**	**Amount (kg)**
Cellulose	479.1589	-	479.1589
Hemicellulose	376.9441	-	376.9441
Lignin and Others	338.7570	-	338.7570
Water	349.6684	0.1189	349.7873
Sulphuric Acid	-	0.0132	0.0132
Total	1544.5784	0.1321	1544.7105
Total Input = 1544.7105			Total Output = 1544.7105

6.4 STAGE 4: PFR REACTOR

Table 6.4 Modified Material balance over PFR

Materials	**Input**	**Output**
	G	**H**
	Amount (kg)	**Amount (kg)**
Cellulose	479.1589	455.2016
Hemicellulose	376.9441	37.6994
Lignin and Others	338.7570	338.7570
Water	349.7873	442.3922
Sulphuric Acid	0.0132	0.0132
Furfural	-	246.6898
CDP	-	23.9573
Total	1544.7105	1544.7105
Total Input = 1544.7105kg		Total Output =1544.7105kg

6.5 STAGE 5 ADDITION OF NaOH

Table 6.5 Modified Material balance due to addition of NaOH

Material	**Input**		**Output**
	H	**I**	**J**
	Amount (kg)	**Amount (kg)**	**Amount (kg)**
Furfural	246.6898	-	246.6898
Water	442.3922	0.1195	442.5167
CDP	23.9573	-	23.9573
Cellulose	455.2016	-	455.2016
Hemicellulose	37.6994	-	37.6994
Lignin & others	338.7570	-	338.7570
Na_2SO_4	-	-	0.0191
NaOH	-	0.0113	0.0004

H_2SO_4	0.0132	-	-
Total	1544.7105	0.1308	1544.8413
Total Input = 1544.8413kg			Total = 1544.8413kg

6.6 STAGE 6: EXPANSION VESSEL

Table 6.6 Modified Material balance over expansion vessel

Material	**Input**	**Output**	
	J	**K**	**L**
	Amount (kg)	**Amount (kg)**	**Amount (kg)**
Furfural	246.6898	4.9343	241.7555
Water	442.5167	359.1489	83.3678
CDP	23.9573	0.4541	23.5032
Cellulose	455.2016	455.2016	-
Hemicellulose	37.6994	37.6994	-
Lignin & others	338.7570	338.7570	-
Na_2SO_4	0.0191	0.0191	-
NaOH	0.0004	0.0004	-
Total	1544.8413	1196.2146	348.6267
Total Input = 1544.8413kg		Total = 1544.8413kg	

6.7 STAGE 7: DISTILLATION COLUMN

Table 6.7 Modified Material balance over distillation column

Material	**Input**	**Output**	
	L	**M**	**N**
	Amount (kg)	**Amount (kg)**	**Amount (kg)**
Furfural	241.7555	12.0874	229.6681
Water	83.3678	61.6846	21.6832
CDP	23.5032	22.3046	1.1986
Total	348.6267	96.0766	252.5499

Total Input = 348.6267kg	Total Output = 348.6267kg

6.8 OVERALL MODIFIED MATERIAL BALANCE

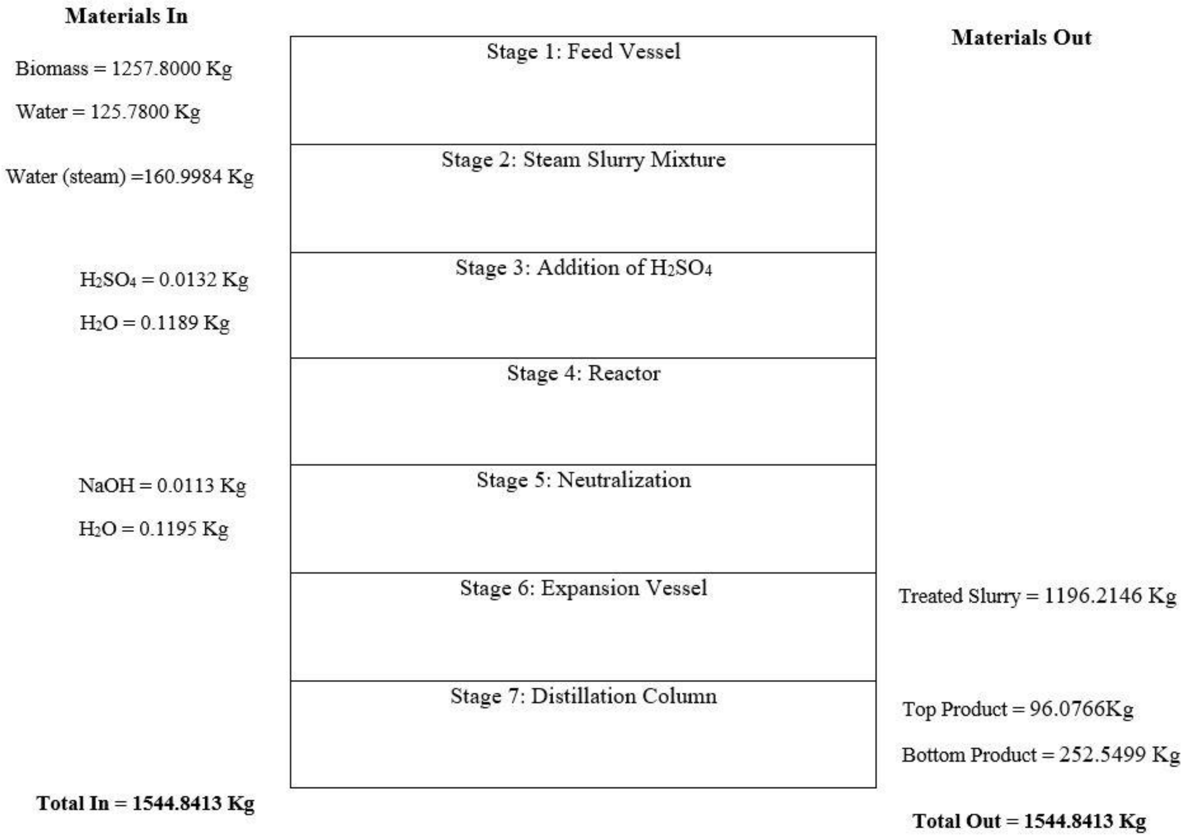

Fig 6.1 Overall modified material balance.

6.9 MODIFIED MATERIAL BALANCE0020FLOWCHART

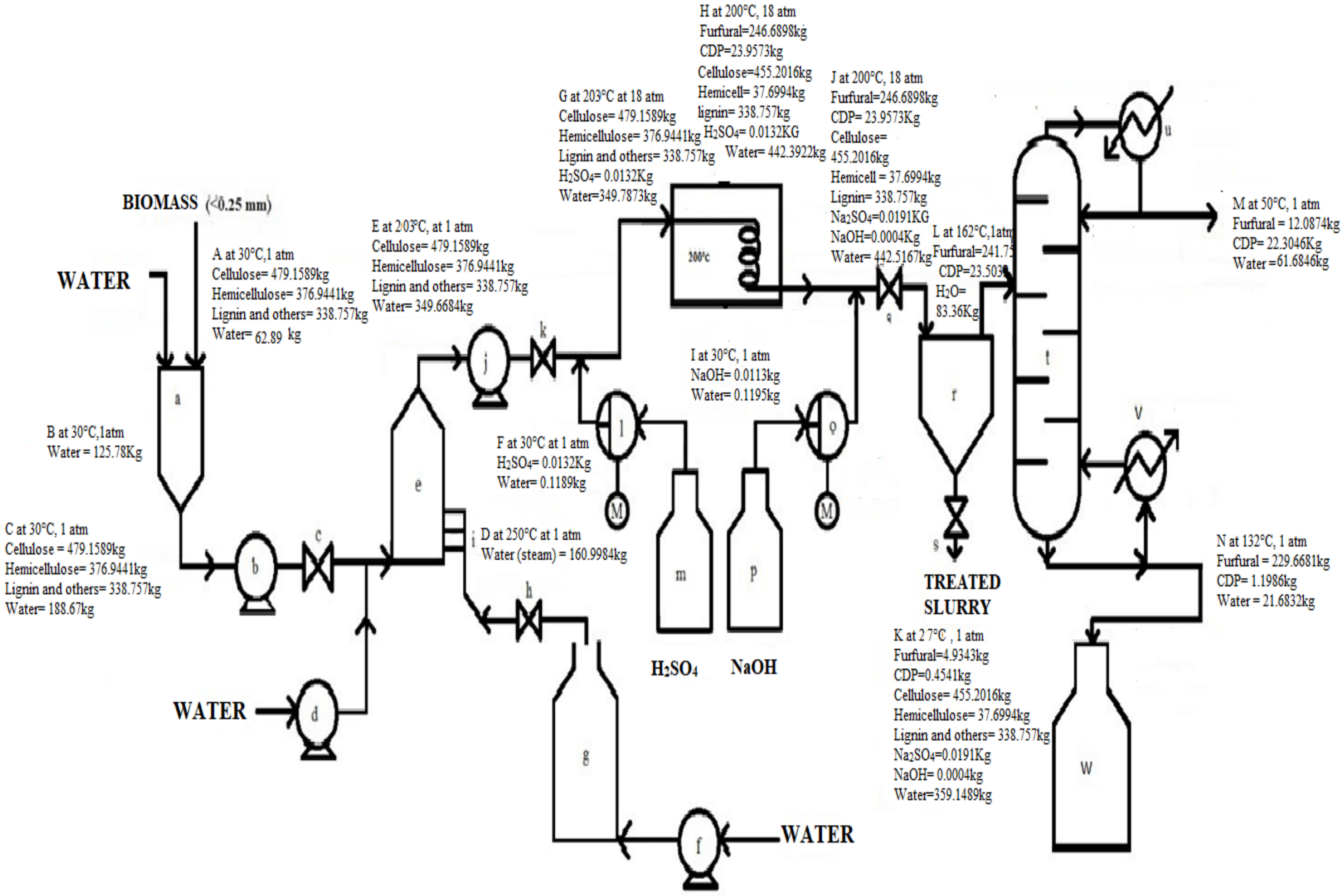

Fig 6.2 Modified Material Balance Flowchart.

CHAPTER 7

ENERGY BALANCE

OVERALL ASSUMPTIONS:

1. Energy balance is calculated on hourly basis.
2. Datum temperature of 25 °C has been taken in all energy balance calculations.
3. There is no heat loss in any equipment by conduction, convection, or radiation.
4. Ambient temperature is assumed to be 25 °C.

DATA:

Specific Heat Values:

1. The specific heat value for cellulose is, $C_{P_{\text{Cellulose}}}$ = 1.3388 KJ/kg-K [6]
2. The specific heat value for hemicellulose is, $C_{P_{\text{Hemicellulose}}}$ = 1.4 KJ/kg-K [7]
3. The specific heat value for lignin with impurities is, $C_{P_{\text{Lignin}}}$ = 1.10 KJ/ kg-K [8]
4. The specific heat value for water is, $C_{P_{\text{Water}}}$ = 4.1785 KJ/ kg-K [9]
5. The specific heat value of steam, $C_{P_{\text{Steam}}}$ = 1.9892 KJ/kg-K [10]
6. The specific heat value for H_2SO_4 at 30 °C, 10 % $\frac{wt}{wt}$ is, $C_{P_{H_2SO_4}}$ = 3.8342 KJ/ kg-K [9]
7. The specific heat value for furfural is, $C_{P_{\text{Furfural}}}$ = 1.66 KJ/kg-K [13]
8. The specific heat value for NaOH at 30 °C 9% $\frac{wt}{wt}$ is, $C_{P_{\text{NaOH}}}$ = 3.49364 KJ/kg-K [14]
9. The specific heat value for Na_2SO_4 is, $C_{P_{Na_2SO_4}}$ = 0.9665 KJ/kg-K [15]

Table 7.1 C_P values of different components.

Components	C_P (KJ/kg-K)
Cellulose	1.3388
Hemicellulose	1.40
Lignin	1.10
Water	4.1785
Steam	1.9892
H_2SO_4	3.8342
Furfural	1.66
NaOH	3.49364
Na_2SO_4	0.9665

<u>Heat of Formation</u>:

1. The heat of formation for hemicellulose at 25 °C, $\Delta_f H_{Hemicellulose}$ = -762.9 KJ/kmole [16]
2. The heat of formation for furfural at 25 °C, $\Delta_f H_{Furfural}$ = -200.2 KJ/kmole [13]
3. The heat of formation for H_2SO_4 at 25 °C, $\Delta_f H_{H_2SO_4}$ = -909.27 KJ/kmole [11]
4. The heat of formation for water at 25 °C, $\Delta_f H_{Water}$ = -285.84 KJ/kmole [11]
5. The heat of formation for NaOH at 25 °C, $\Delta_f H_{NaOH}$ = -470.09 KJ/kmole [11]
6. The heat of formation for Na_2SO_4 at 25 °C, $\Delta_f H_{Na_2SO_4}$ = -1389.47 KJ/kmole [11]

(Ref: Perry's Handbook 7th Ed.; Table 2-220)

Table 7.2 $\Delta_f H$ values of different components at 25 °C.

Components	$\Delta_f H$ (KJ/kmole)	$\Delta_f H$ for 2.5013 mole (KJ)
Hemicellulose	-762.9	-1908241.77
Furfural	-200.2	-500760.26
H_2SO_4	-909.27	-227457.051

Water	-285.84	-716971.592
NaOH	-470.09	-1175836.117
Na_2SO_4	-1389.47	-3475481.311

Heat of Reaction:

For Furfural:

1. ΔH_{rxn}^{298} = -8980 KJ/mole
2. ΔH_{rxn}^{473} = 19618.20189 KJ

For Na_2SO_4:

1. ΔH_{rxn}^{298} = -111.68 KJ/mol
2. ΔH_{rxn}^{473} = -22.9391 KJ

Latent heat of Vaporization:

1. Latent Heat of Vaporization for Furfural, $\lambda^{Furfural}$ = 444 KJ/kg [13]
2. Latent Heat of Vaporization for Water, λ^{H_2O} = 2250 KJ/kg [11]
3. Latent Heat of Vaporization for CDP, λ^{CDP} = 712.5 KJ/kg [17]

Table 7.3 Latent Heat of Vaporization of different components.

Component	**Latent Heat of Vaporization (KJ/kg)**
Furfural	444
Water	2250
CDP	712.5

7.1 STAGE 1: FEED VESSEL

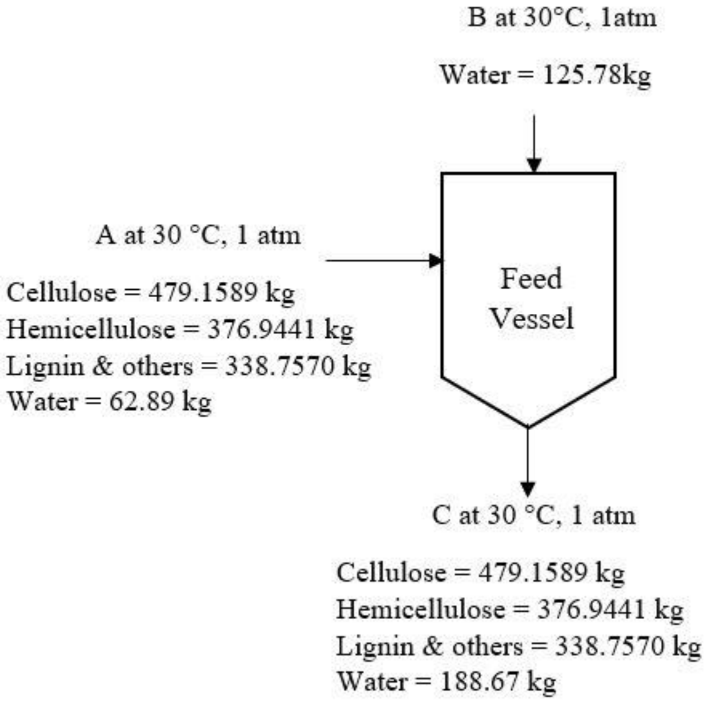

Fig. 7.1 Energy balance over feed vessel.

The feed vessel is fed with A, which is a mixture of cellulose, hemicellulose, lignin, and other impurities, and with B, which is water.

Calculation of $C_{P_{avg}}$:

For stream A,

$$C_{P_A} = \frac{\Sigma miCpi}{m}$$

$$C_{P_A} = \frac{479.1589 \times 1.3388}{1257.8} + \frac{376.9441 \times 1.4}{1257.8} + \frac{338.757 \times 1.1}{1257.8} + \frac{62.89 \times 4.1785}{1257.8}$$

C_{P_A} = 1.4347 KJ/kg-K

For stream B,

C_{P_B} = 4.1785 KJ/kg-K

For stream C,

$$C_{P_C} = \frac{\Sigma miCpi}{m}$$

$$C_{P_C} = \frac{1257.8 \times 1.4347}{1383.58} + \frac{125.78 \times 4.1785}{1383.58}$$

C_{P_C} = 1.6841 KJ/kg-K

Energy in:

Amount = $H_A + H_B$

= $[mC_PdT]_A + [mC_PdT]_B$

= [1257.8 × 1.4347 × (303 – 298)] + [125.78 × 4.1785 × (303 – 298)]

= 9022.8283 + 2627.85865

= 11650.68695 KJ

Energy out:

Amount = H_C

= $[mC_PdT]_C$

= 1383.58 × 1.6841 × (303 – 298)

= 11650.43539 KJ

Table 7.4 Energy balance over the feed vessel

Streams	Weight (Kg)	$C_{p\ avg}$ (KJ/KgK)	Temp difference(K)	mC_pdt (KJ)
A	1257.8	1.4347	303-298=5	H_A = 9022.8283
B	125.78	4.1785	303-298=5	H_B = 2627.85865
INPUT				11650.68695
C	1383.58	1.6841	303-298=5	H_C =11650.43539
OUTPUT				11650.43539

7.2 STAGE 2: STEAM-SLURRY MIXTURE

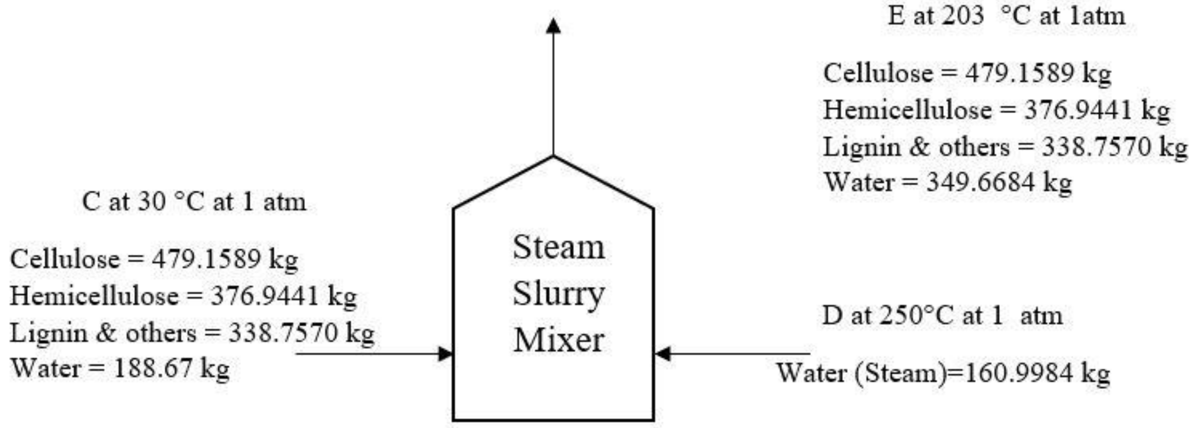

Fig. 7.2 Energy Balance over the steam-slurry mixture.

The output (C) from the feed vessel is now the input for the steam-slurry mixture. The steam-slurry mixture is also fed with steam (D) and the output (E) from steam-slurry mixture is sent for to the next stage.

The output, E contains a mixture of cellulose, hemicellulose, lignin with other impurities, and water.

Calculation of $C_{P_{avg}}$:

For stream D,

C_{P_D} =1.9892 KJ/kg-K

For stream E,

$$C_{P_E} = \frac{\Sigma miCpi}{m}$$

$$C_{P_E} = \frac{1383.58 \times 1.6841}{1544.5784} + \frac{160.9984 \times 1.9892}{1544.5784}$$

C_{P_E} = 1.718172 KJ/kg-K

Energy in:

Amount = $H_C + H_D$

$= [mC_PdT]_C + m[C_{P_{H_2O}}dT + \lambda^{H_20} + C_{P_{steam}}dT]$

= [1383.58 × 1.6841 × (303 – 298)] + 160.99847[4.1785 × (100 – 25) + 2250 + 1.9892 × (250 – 100)]

= 472385.4241 KJ

Energy out:

Amount = H_E

$= [mC_PdT]_E$

= 1544.5784 × 1.718172 × (476 – 178)

= 472385.5418 KJ

Table 7.5 Energy balance over steam-slurry mixture

Streams	Weight (kg)	$C_{p\ avg}$ (KJ/KgK)	Sensible Heat at 100^0C for 1 kg (KJ/Kg)	Latent heat at 100^0C (KJ/Kg)	Super heat at 100^0C for 1 kg (KJ/kg)	Temperature difference (K)	mC_pdt (KJ)
C	1383.58	1.6841				303-298 = 5	H_C=11650.43539
D	160.9984		313.3878	2250	298.38		H_D=460734.9887
		INPUT					472385.4241
E	1544.5784	1.718172				476-298 = 178	H_E= 472385.5418
OUTPUT							472385.5418

7.3 STAGE 3: ADDITION OF H_2SO_4

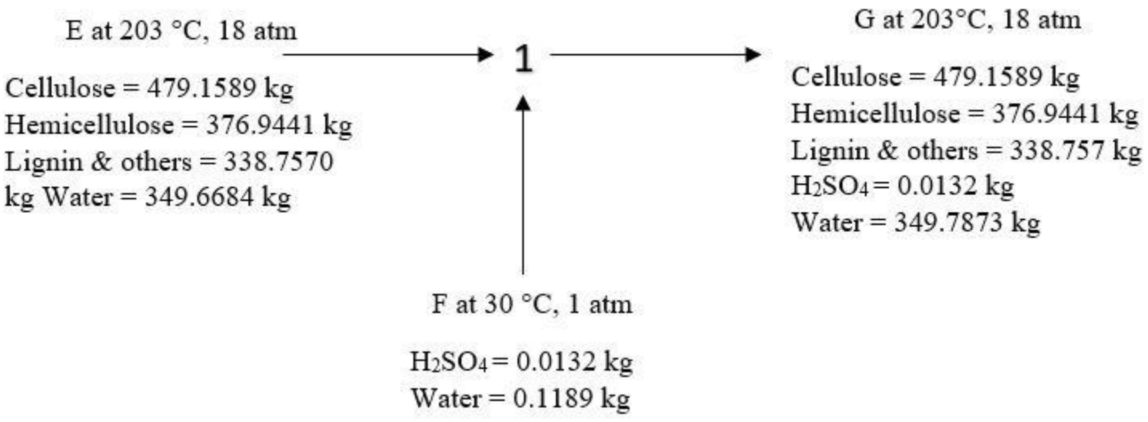

Fig. 7.3 Energy Balance due to addition of H_2SO_4

The output (E) from steam-slurry mixture is mixed with small amount of H_2SO_4 (F) to act as a catalyst, and the mixture (G) contains a mixture of cellulose, hemicellulose, lignin with other impurities, water, and H_2SO_4.

Calculation of $C_{P_{avg}}$:

For stream G,

$$C_{P_G} = \frac{\Sigma miCpi}{m}$$

$$C_{P_G} = \frac{1544.5784 \times 1.718172}{1544.7105} + \frac{0.1321 \times 3.8342}{1544.7105}$$

C_{P_G} = 1.718035 KJ/kg-K

Energy in:

Amount = $H_E + H_F$

= $[mC_PdT]_E + [mC_PdT]_F$

= [1544.5784 × 1.718172 (476 – 298)] + [0.1321 × 3.8342 × (303 – 298)]

= 472388.0743 KJ

Energy out:

Amount = H_G

= $[mC_PdT]_G$

= [1544.7105 × 1.718035 × (476 – 298)]

= 472388.2733 KJ

Table 7.6 Energy balance due to addition of H_2SO_4

Streams	Weight (kg)	$C_{p\,avg}$ (KJ/KgK)	Temp Difference (K)	mC_pdt (KJ)
E	1544.5784	1.718172	476-298 = 178	H_E= 472385.5418
F	0.1321	3.8342	303-298= 5	H_F= 2.5325
INPUT				472388.0743
G	1544.7105	1.718035	476-298=178	H_G = 472388.2733
OUTPUT				472388.2733

7.4 STAGE 4: PFR REACTOR

The stream G is now fed into a reactor where reaction takes place as

$$(C_5H_80_4)_n \longrightarrow n\ C_5H_4O_2 + 2n\ H_2O$$

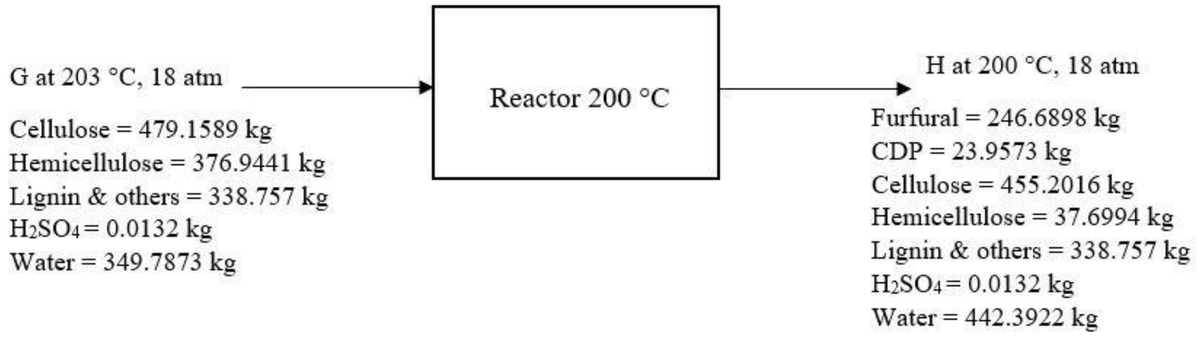

Fig. 7.4 Energy Balance during reaction

Calculation of $C_{P_{avg}}$:

For stream H,

$$C_{P_H} = \frac{\Sigma miCpi}{m}$$

$$C_{P_H} = \frac{455.2016 \times 1.3388}{1544.7105} + \frac{37.6994 \times 1.4}{1544.7105} + \frac{338.7570 \times 1.1}{1544.7105} +$$

$$\frac{442.3922 \times 1.9892}{1544.7105} + \frac{0.1321 \times 3.8342}{1544.7105} + \frac{246.6898 \times 1.66}{1544.7105} +$$

$$\frac{23.9573 \times 3.8525}{1544.7105}$$

C_{P_H} = 1.5646 KJ/kg-K

Energy in:

H_G = 472388.2733 KJ

Energy out:

$H_H = m\, C_{P_H} dT$

H_H = 1544.7105 × 1.5646 × (200 – 25)

H_H = 422949.45875 KJ

The heat of reaction is given as

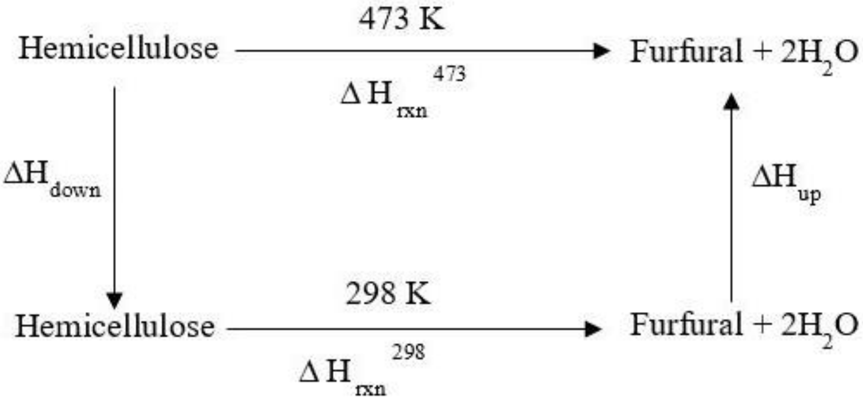

Fig. 7.5 Heat of reaction for furfural

No of moles reacted = 12.5784 × 0.2043 = 2.5013 kmole = × 2.5013 × 10^3 moles

$\Delta_f H_{Hemicellulose} = -762.9 \times 2.5013 \times 10^3 = -1908241.77$ KJ

$\Delta_f H_{Furfural} = -200.2 \times 2.5013 \times 10^3 = -500760.26$ KJ

$\Delta_f H_{Water} = -285.84 \times 2.5013 \times 10^3 = -714971.592$ KJ

$\Delta H_{rxn}^{298} = \Delta_f H_{Product} - \Delta_f H_{Reactant}$

$\Delta H_{rxn}^{298} = [-500760.26 + 2(-714971.592)] - [-1908241.77]$

$\Delta H_{rxn}^{298} = -22461.674$ KJ

$C_{P_{down}} = C_{P_{Hemicellulose}} = 1.4$ KJ/kg-K

$C_{P_{up}} = C_{P_{Furfural + Water}} = \frac{246.6898 \times 1.66}{246.6896 + 92.5549} + \frac{92.5549 \times 4.1785}{246.6898 + 92.5549}$

$C_{P_{up}} = 2.1088$ KJ/kg-K

$H_{up} = (246.6898 + 92.5549) \times 2.1088 \times (200 - 25)$

$H_{up} = 125194.8272$ KJ

$H_{down} = (376.9441 - 37.6994) \times 1.4 \times (25 - 200)$

$H_{down} = -83114.9515$ KJ

$\Delta H_{rxn}^{473} = \Delta H_{down} + \Delta H_{rxn}^{298} + H_{up}$

$\Delta H_{rxn}^{473} = -83114.9515 - 22461.674 + 125194.8272$

$\Delta H_{rxn}^{473} = 19618.20179$ KJ

The reactor is kept at a constant temperature of 473 K (203 °C). Let, the mass flow rate of water required in the cooling jacket is m. Therefore,

Input + Generation = Output + Removed

$H_G + \Delta H_{rxn}^{473} = H_H$ + Removed

472388.2733 + 19618.20179 = 422949.45875 + Removed

Removed = 69056.81734 KJ

mC_PdT = 69056.81734

m × 4.1785 × (80 – 25) = 69056.81734

m = 330.4855 kg/h

Table 7.7 Energy balance over PFR

Streams	**Weight (Kg)**	**C_p (KJ/kgK)**	**Temp Difference(K)**	**mC_pdt (KJ)**
G	1544.7105	1.718035	476-298=178	H_G = 472388.2733
INPUT				472388.2733
H	1544.7105	1.5646	473-298= 175	H_H = 422949.45875
OUTPUT				422949.45875
GENERATION				1918.20179
REMOVED				69056.81734

7.5 STAGE 5: ADDITION OF NaOH

A small amount of NaOH (I) is added to the output stream from the reactor (H) to neutralize the excess amount of acid present to get stream (J) where following reactions take place.

$$2\ NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ H_2O$$

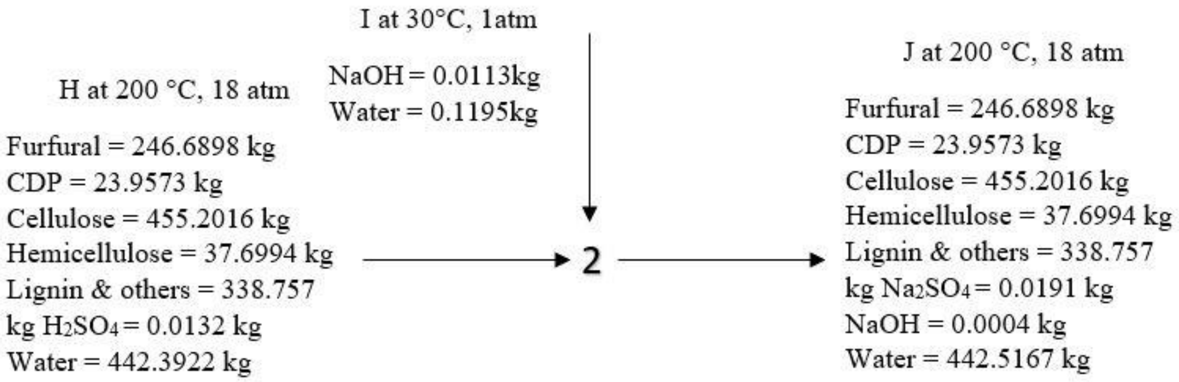

Fig. 7.6 Energy balance due to addition of NaOH.

Calculation of $C_{P_{avg}}$:

For stream I,

$C_{P_{NaOH}}$ = 3.49364 KJ/kg-K

For stream J,

$$C_{P_J} = \frac{\Sigma miCpi}{m}$$

$$C_{P_J} = \frac{1544.7105 \times 1.5646}{1544.8413} + \frac{0.1308 \times 3.49364}{1544.8413}$$

C_{P_J} = 1.56439 KJ/kg-K

Energy in:

Amount = $H_H + H_I$

= $[mC_PdT]_H + [mC_PdT]_I$

= 472388.2733 + [0.1308 × 3.49364 × (30 – 25)]

= 422951.7436 KJ

<u>Energy out</u>:

Amount = H_J

= $[mC_PdT]_J$

= 1544.8413 × 1.56439 × (200 – 25)

= 422928.4992 KJ

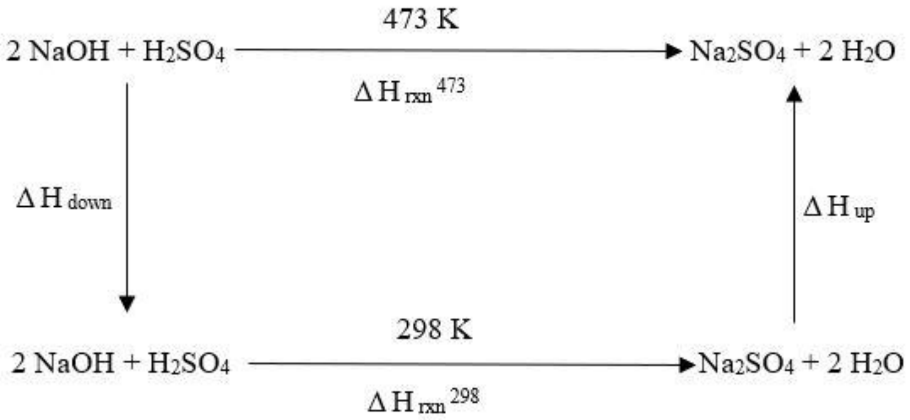

Fig. 7.7 Heat of reaction for Na_2SO_4

No of moles reacted = 1.0714×10^{-5} kmole = 1.0714×10^{-2} moles

$\Delta H_{rxn}{}^{298} = \Delta_f H_{Product} - \Delta_f H_{Reactant}$

$\Delta H_{rxn}{}^{298} = [2(-285.83) + (-1389.47)] - [(-909.27) + 2(-470.09)]$

$\Delta H_{rxn}{}^{298} = -111.86$ KJ/mol

$\Delta H_{rxn}{}^{298} = -111.86 \times 1.0714 \times 10^{-2}$

$\Delta H_{rxn}{}^{298} = -1.1965$ KJ

$$C_{P_{down}} = C_{P_{H_2SO_4 + NaOH}} = \frac{0.1321 \times 3.8342}{0.1321+0.1304} + \frac{0.1304 \times 3.49364}{0.1321+0.1304}$$

Cp_{down} = 3.6731 KJ/kg-K

Cp_{up} = $Cp_{Na_2SO_4 + H_2O}$ = $\frac{0.2434 \times 4.1785}{0.2434 + 0.0191} + \frac{0.0191 \times 0.9665}{0.2434+0.0191}$

Cp_{up} = 3.1477 KJ/kg-K

H_{up} = (0.2434 + 0.0191) × 3.1477 × (200 – 25)

H_{up} = 144.5994 KJ

H_{down} = (0.1321 + 0.1304) × 3.6731 × (25 – 200)

H_{down} = - 168.735 KJ

ΔH_{rxn}^{473} = H_{down} + ΔH_{rxn}^{298} + H_{up}

ΔH_{rxn}^{473} = - 168.735 – 1.1965 + 144.5994

ΔH_{rxn}^{473} = - 22.9391 KJ

During the neutralization reaction, some heat will generate. Therefore,

Input + Generation = Output

Output = H_H +H_I + ΔH_{rxn}^{473}

Output = 422951.7436 – 22.9391

Output = 422928.4992 KJ = H_J

Table 7.8 Energy balance due to addition of NaOH

Streams	Weight (kg)	C_p (KJ/kgK)	Temp Difference(K)	mC_pdt (KJ)
H	1544.7105	1.5646	473-298= 175	H_H = 422949.45875
I	0.1308	3.49364	303-298=5	H_I = 2.2848

INPUT				422951.7436
J	1544.8413	1.56439	473-298= 175	H_J = 422928.4992
OUTPUT				422928.4992
GENERATION				-22.9391

7.6 STAGE 6: EXPANSION VESSEL

The stream (J) after neutralization reaction contains furfural, water, some amount of methanol, ethanol, acetic acid, formic acid (which is collectively called as cellulose dehydrated product, CDP), lignin and other impurities, some unreacted NaOH, and Na_2SO_4.

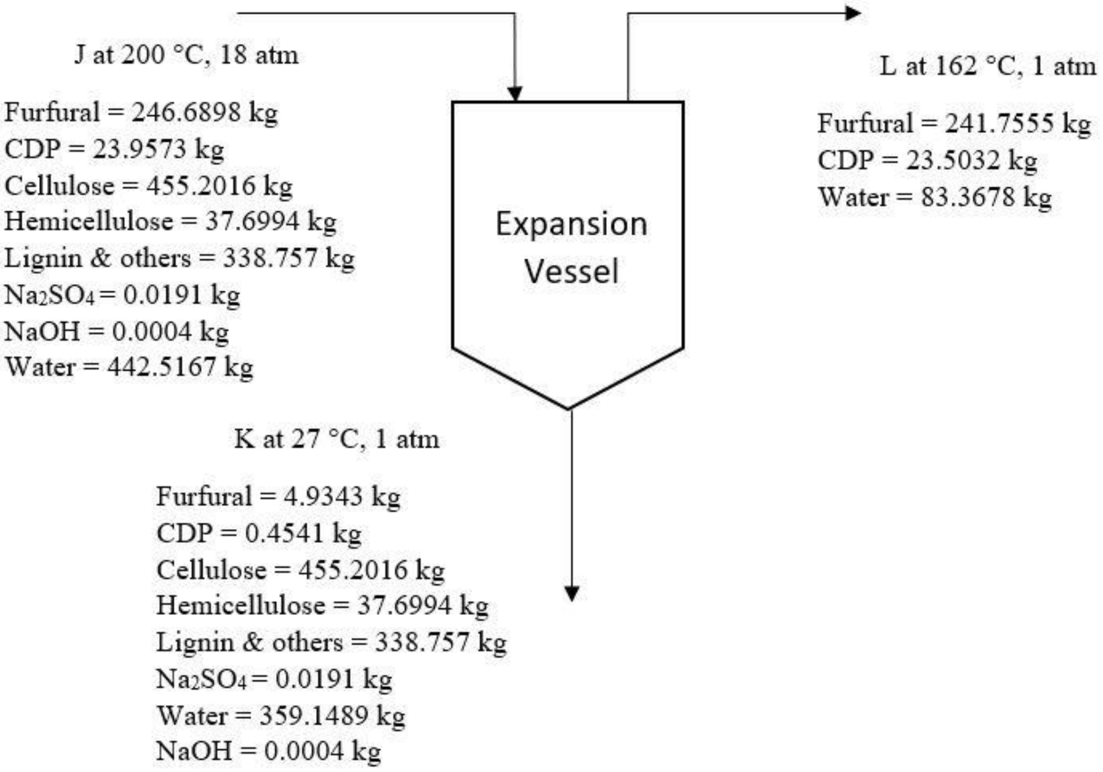

Fig. 7.8 Energy balance over expansion vessel.

The stream J enters in the expansion vessel in which the first separation takes place.

Components like furfural, water and CDP will boil upon flashing and turn into vapours. The left out components such as lignin, Na_2SO_4, NaOH, etc. will not vaporize.

Calculation of $C_{P_{avg}}$:

For stream K,

$$C_{P_K} = \frac{\Sigma miCpi}{m}$$

$$C_{P_K} = \frac{4.9394 \times 1.66}{1196.2146} + \frac{0.4541 \times 3.8525}{1196.2146} + \frac{455.2016 \times 1.3388}{1196.2146} + \frac{37.6994 \times 1.4}{1196.2146}$$

$$+ \frac{0.0191 \times 0.9665}{1196.2146} + \frac{0.0004 \times 3.49364}{1196.2146} + \frac{359.1489 \times 4.1785}{1196.2146} +$$

$$\frac{338.757 \times 1.1}{1196.2146}$$

C_{P_K} = 3.1035 KJ/kg-K

Table 7.9 Sensible heat and Latent heat of components for expansion vessel

Components	ΔT (Sensible Heat) (K)	ΔT(Super Heat) (K)
Furfural	434.7 – 298 = 136.7	435 – 434.7 = 0.3
CDP	362.34 – 298 = 64.34	435 – 362.34 = 71.66
Water	373 – 298 = 75	435 – 373 = 62

$H_{Furfural}$ = 241.755 [{1.66 × (161.7 – 25)} + 444 + {1.66 × (162 – 161.7)}]

$H_{Furfural}$ = 162319.1421 KJ

H_{CDP} = 23.5032 [{3.8525 × (89.34 – 25)} + 712.5 + {3.8525 × (162 – 89.34)}]

H_{CDP} = 29150.8427 KJ

H_{H_2O} = 83.3678 [{4.1785 × (100 – 25)} + 2250 + {1.9892 × (162 – 100)}]

H_{H_2O} = 223938.2076 KJ

$H_L = H_{Furfural} + H_{CDP} + H_{H_2O}$

H_L = 415408.1924 KJ

<u>Energy in</u>:

Amount = H_J

= 422928.4992 KJ

<u>Energy out</u>:

Amount = $H_K + H_L$

= $[mC_PdT]_K$ + 415408.1924

= 1996.2146 × 3.1035 × (27 – 25) + 415408.1924

= 422928.7936 KJ

Table 7.10 Energy balance over expansion vessel.

Streams	**Weight(kg)**	**C_P (KJ/kgK)**	**Temp Difference(K)**	**mC_Pdt (KJ)**
J	1544.8413	1.56439	473-298= 175	H_J = 422928.4992
INPUT				422928.4992
K	1196.2146	3.1035	300-298= 2	H_K = 7520.6012
L				$H_L = H_1 + H_2 + H_3$ =415408.1924

OUTPUT	422928.7936

7.7 STAGE 7: DISTILLATION COLUMN

After the streams have been separated using an expansion vessel, the volatile stream (L), consisting of furfural, water, and CDP is now fed to a distillation column where furfural is separated out from the rest of the components.

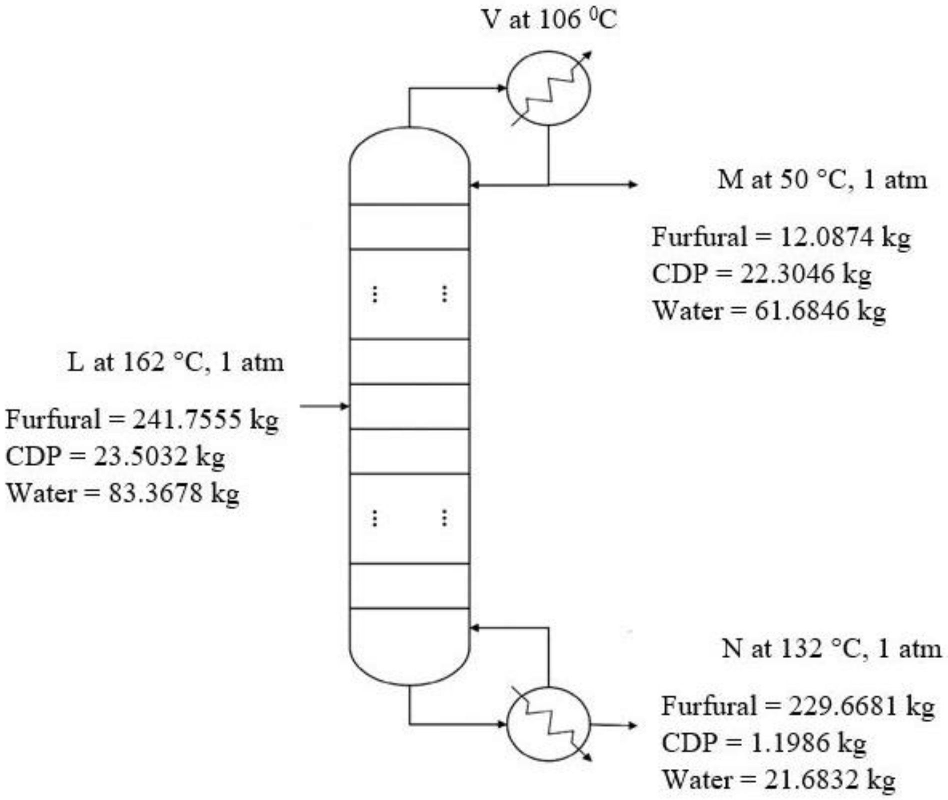

Fig. 7.9 Energy balance over distillation column.

Calculation of $C_{P_{avg}}$:

For stream M,

$$C_{P_M} = \frac{\Sigma miCpi}{m}$$

$$C_{P_M} = \frac{12.0874 \times 1.66}{96.0766} + \frac{61.6846 \times 4.1785}{96.0766} + \frac{22.3046 \times 3.8525}{96.0766}$$

C_{P_M} = 3.785 KJ/kg-K = C_{L_R}

For stream N,

$$C_{P_N} = \frac{\Sigma miCpi}{m}$$

$$C_{P_N} = \frac{229.6681 \times 1.66}{252.5499} + \frac{21.6832 \times 4.1785}{252.5499} + \frac{1.1986 \times 3.8525}{252.5499}$$

C_{P_N} = 1.8866 KJ/kg-K

Assuming Reflux Ratio (R) = 1.5

Tower top temperature = 106 ^{0}C

Tower bottom temperature = 132 ^{0}C

Table 7.11 Sensible heat and Latent heat of components for distillation column

Components	**ΔT (Sensible Heat) (K)**	**ΔT(Super Heat) (K)**
Furfural	379 – 298 = 81	-
CDP	362.34 – 298 = 64.34	379 – 362.34 = 16.66
Water	373 – 298 = 75	379 – 373 = 6

H_M = 96.0766 × 3.785 × (50 – 25)

H_M = 9091.2483 KJ

$H_N = 252.5499 \times 1.8866 \times (132 - 25)$

$H_N = 50981.2886$ KJ

$R = 1.5$

$\frac{L_R}{M} = 1.5$

$L_R = 1.5\ M$

$L_R = 1.5 \times 96.0766$

$L_R = 144.1149$ kg/h

And,

$V = L_R + M$

$V = 144.1149 + 96.0766$

$V = 240.1915$ kg/h

$H_{Furfural} = 12.0874 \times 1.66 \times (106 - 25)$

$H_{Furfural} = 1625.2718$ KJ

$H_{H_2O} = 61.6846\ [\{4.1785 \times (100 - 25)\} + 2250 + \{1.9895 \times (106 - 100)\}]$

$H_{H_2O} = 158857.8617$ KJ

$H_{CDP} = 22.3046\ [\{3.8525 \times (89.34 - 25)\} + 712.5 + \{3.8525 \times (106 - 89.34)\}]$

$H_{CDP} = 22852.2337$ KJ

$H_V = H_{Furfural} + H_{H_2O} + H_{CDP}$

$H_V = 1625.2718 + 158857.8617 + 22852.2337$

H_V = 183335.3672 KJ

H_{L_R} = 144.1149 × 3.785 × (106 – 50)

H_{L_R} = 30546.5942 KJ

$Q_C = H_V – H_M – H_{L_R}$

Q_C = 183335.3672 – 9091.2483 – 30546.5942

Q_C = 143697.5247 KJ

$Q_B = H_L – Q_C – H_M - H_N$

Q_B = 415408.1924 – 143697.5247 – 9091.2483 – 50981.2886

Q_B = 211638.1308 KJ

$H_L = H_M + H_N + Q_C + Q_B$

H_L = 9091.2483+ 50981.2886 + 143697.5247 + 211638.1308

H_L = 415408.1924 KJ

Table 7.12 Energy balance over distillation column

Streams	Weight (Kg)	C_p (KJ/kgK)	Temp Difference(K)	mC_pdt (KJ)
L				$H_L = H_1+H_2+H_3$ =415408.1924
INPUT				415408.1924
M	96.0766	3.785	323-298=25	H_M = 9091.2483
N	252.5499	1.8866	405-298=107	H_N = 50981.2886

OUTPUT	$H_M + H_N + Q_C + Q_B$ = 415408.1924

The amount of water, m_C required in the condenser can be calculated as

$Q_C = m_C \times C_{P_{Water}} \times (60 - 25)$

$143697.5247 = m_C \times 4.18 \times 35$

$m_C = 982.21$ kg

The amount of steam, m_B required in the reboiler at 100 °C is

$Q_B = mB \times \lambda^{H_2O}$

$211638.1308 = m_B \times 2250$

$m_B = 94.06$ kg

7.8 ENERGY BALANCE FLOWCHART

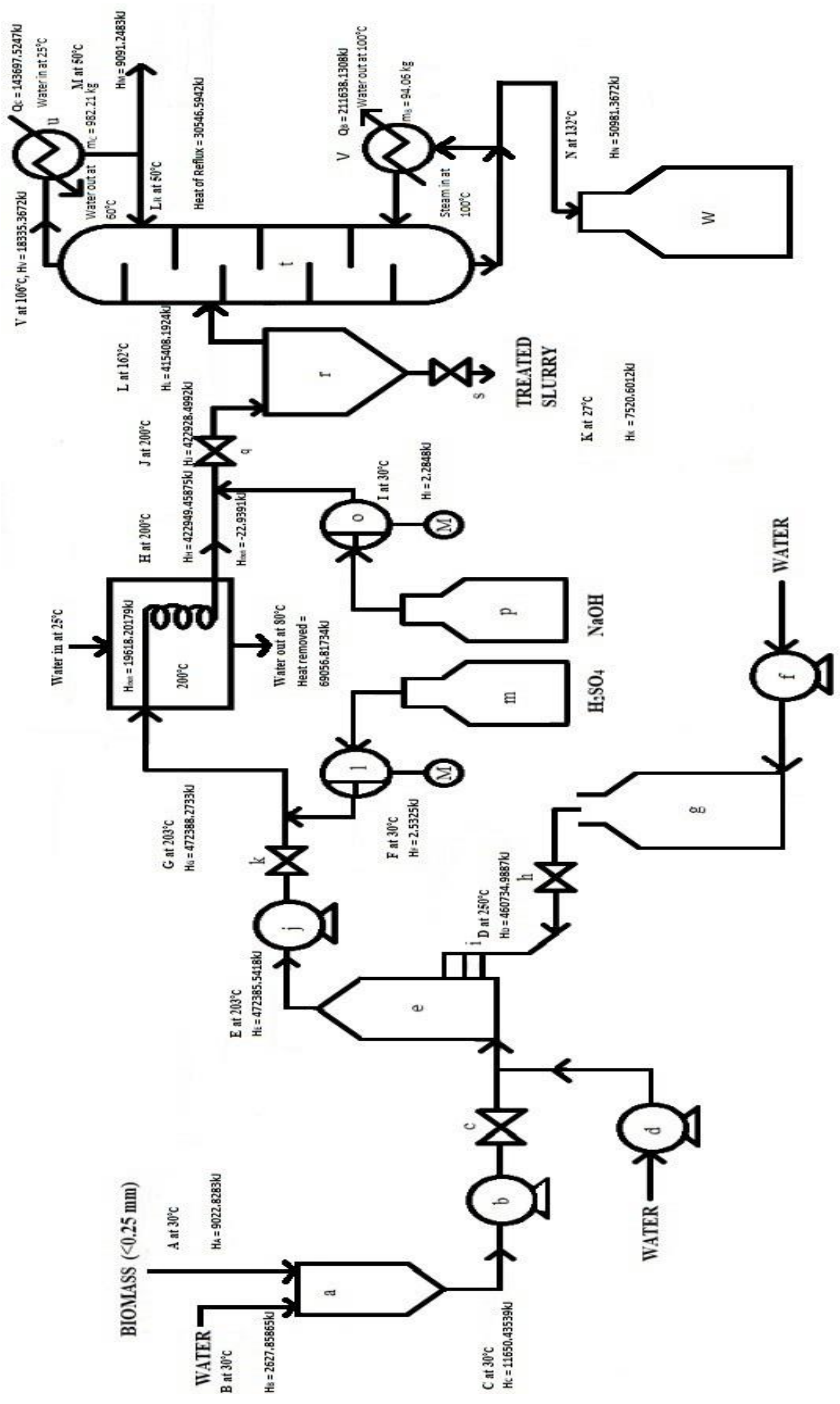

Fig 7.10 Energy Balance Flowchart

CHAPTER 8

DESIGN OF EQUIPMENT

8.1 DESIGN OF DISTILLATION COLUMN

Data:

1. P = 1 atm = 760 mm Hg.
2. Density of furfural, $\rho_{Furfural}$ = 1160 kg/m^3 [19]
3. Density of water, ρ_{Water} = 997 kg/m^3 [18]
4. Density of CDP, ρ_{CDP} = 789 kg/m^3 [19]
5. Molecular mass of furfural = 96.08 kg/kmol [20]
6. Molecular mass of water = 18 kg/kmol [20]
7. Molecular mass of CDP = 46.46 kg/kmol
8. Universal Gas Constant (R) = 0.082058 m3-atm/kmol-K

Taking base component = Furfural (A) = Heavy Key

Vapor pressure data are calculated using Antoine equation. [21]

8.1.1 Tower Top Temperature Calculation

Trial 1:

T = 161.7 °C

Table 8.1 Trial 1

Component	x_{Mi}	P^V (mm Hg)	$K_i = P^V/P$	α_i	α_i/x_i
(HK) Furfural (A)	0.03	764.71	1.01	1	0.03
(LK) Water (B)	0.85	4294	5.65	5.59	0.152
CDP (C)	0.12	10143.82	13.34	13.21	0.0091

$K_C = \Sigma \frac{\alpha_i}{x_i}$

$K_C = 0.1911$

$P^V = 0.1911 \times 760$

$P^V = 145.236$ mm Hg

T = 108.76 °C ≠ 161.7 °C

<u>Trial 2</u>:

T = 108.76 °C

Table 8.2 Trial 2

Component	x_{Mi}	P^V (mm Hg)	$K_i = P^V/P$	α_i	α_i/x_i
(HK) Furfural (A)	0.03	134.15	0.1765	1	0.03
(LK) Water (B)	0.85	961.21	1.265	7.17	0.118
CDP (C)	0.12	2116.72	2.785	15.78	0.0076

$K_C = \Sigma \frac{\alpha_i}{x_i}$

$K_C = 0.1556$

$P^V = 0.1556 \times 760$

P^V = 145.236 mm Hg

T = 103.30 °C ≠ 108.76°C

Trial 3:

T = 103.30 °C

Table 8.3 Trial 3

Component	**x_{Mi}**	**P^V (mm Hg)**	**$K_i = P^V/P$**	**α_i**	**α_i/x_i**
(HK) Furfural (A)	0.03	162.3	0.21	1	0.03
(LK) Water (B)	0.85	1142.97	1.5	7.14	0.132
CDP (C)	0.12	2447.2	3.22	13.18	0.0091

$K_C = \Sigma \frac{\alpha_i}{x_i}$

K_C = 0.1711

P^V = 0.1711 ×760

P^V = 145.236 mm Hg

T = 105.76°C ≠ 103.30°C

Trial 4:

T = 105.76 °C

Table 8.4 Trial 4

Component	**x_{Mi}**	**P^V (mm Hg)**	**$K_i = P^V/P$**	**α_i**	**α_i/x_i**
(HK) Furfural (A)	0.03	134.1	0.176	1	0.03
(LK) Water (B)	0.85	861.41	1.133	6.44	0.1319
CDP (C)	0.12	2046.52	2.692	15.3	0.009

$K_C = \Sigma \frac{\alpha_i}{x_i}$

$K_C = 0.1709$

$P^V = 0.1709 \times 760$

$P^V = 129.884$ mm Hg

T = 105.729 °C ~ 105.76 °C

Tower Top Temperature is 106 °C.

8.1.2 Tower Bottom Temperature Calculation

Trial 1:

T = 161.7 °C

Table 8.5 Trial 1

Component	x_{Ni}	**P^V (mm Hg)**	**$K_i = P^V/P$**	**α_i**	**α_i/x_i**
(HK) Furfural (A)	0.66	764.71	1.01	1	0.66
(LK) Water (B)	0.33	4294	5.65	5.59	1.84
CDP (C)	0.07	10143.82	13.34	13.21	0.9247

$K_c = \frac{1}{\Sigma(\alpha_i x_i)}$

$K_C = \frac{1}{2.8307}$

$K_C = 0.3523$

$P^V = 0.3523 \times 760$

P^V = 268.48 mm Hg

T = 126.14 °C ≠ 161.7 °C

<u>Trial 2</u>:

T = 126.14 °C

Table 8.6 Trial 2

Component	x_{Ni}	**P^V (mm Hg)**	**$K_i = P^V/P$**	**α_i**	**α_i/x_i**
(HK) Furfural (A)	0.66	268.46	0.35	1	0.66
(LK) Water (B)	0.33	784.7	1.035	2.95	0.9742
CDP (C)	0.07	2647.764	3.4839	9.954	0.6968

$K_c = \frac{1}{\Sigma(\alpha_i x_i)}$

$K_C = \frac{1}{2.331}$

K_C = 0.429

P^V = 0.429 × 760

P^V = 326.04 mm Hg

T = 132.14 °C ≠ 126.14 °C

<u>Trial 3</u>:

T = 132.14 °C

Table 8.7 Trial 3

Component	x_{Ni}	**P^V (mm Hg)**	**$K_i = P^V/P$**	**α_i**	**α_i/x_i**
(HK)Furfural (A)	0.66	281.2	0.37	1	0.66

(LK) Water (B)	0.33	846.716	1.1141	3.011	0.9936
CDP (C)	0.07	2831.684	3.7259	10.07	0.7049

$K_c = \frac{1}{\Sigma(\alpha_i x_i)}$

$K_C = \frac{1}{2.3585}$

$K_C = 0.42399$

$P^V = 0.42399 \times 760$

$P^V = 322.23$ mm Hg

T = 131.77 °C ~ 132.14 °C

Tower Bottom Temperature is 132°C.

8.1.3 Number of Stages Calculation

Taking B-A pair i.e., LK-HK pair, we get,

$(\alpha_{BA})_{AVG} = [(\alpha_{BA})_{Top} \times (\alpha_{BA})_{Bottom}]^{0.5}$

$(\alpha_{BA})_{AVG} = [6.44 \times 3.011]^{0.5}$

$(\alpha_{BA})_{AVG} = 4.4035$

Using Fenske Equation, we get,

$N_{min} = \log[(\frac{x_{LK \cdot M}}{x_{HK \cdot N}})(\frac{x_{HK \cdot N}}{x_{LK \cdot M}})] \times \frac{1}{\log(\alpha_{BA})_{AVG}}$

$N_{min} = = \log[(\frac{0.85 \times 0.66}{0.33 \times 0.03})] \times \frac{1}{\log(4.4035)}$

$N_{min} = 2.7234$

$(\alpha_{CA})_{AVG} = [(\alpha_{CA})_{Top} \times (\alpha_{CA})_{Bottom}]^{0.5}$

$(\alpha_{CA})_{AVG} = [15.3 \times 10.07]^{0.5}$

$(\alpha_{CA})_{AVG} = 12.4125$

Table 8.8 Composition Table

Component	**α_{iA}**	**x_L**	**Feed (L)**	**x_M**	**Distillate (M)**	**x_N**	**Bottom Product (N)**
(HK) Furfural (A)	1	0.33	241.7555	0.03	12.0874	0.66	229.6681
(LK) Water (B)	4.4035	0.66	83.3678	0.85	61.6846	0.33	21.6832
CDP (C)	12.4125	0.07	23.5032	0.12	22.3046	0.07	1.1986

For Saturated vapor feed, q = 0

Using Underwood Equation, we get,

$$1 - q = \Sigma \frac{\alpha_{iA} \times x_L}{\alpha_{iA} - \varphi}$$

$$1 - 0 = \frac{1 \times 0.33}{0.33 - \varphi} + \frac{4.4035 \times 0.66}{4.4035 - \varphi} + \frac{12.4125 \times 0.07}{12.4125 - \varphi}$$

For φ = 2.0447, R.H.S of above equation becomes 1.000038 ~ 1 = L.H.S

Again,

$$R_{min} + 1 = \Sigma \frac{\alpha_{iA} \times x_M}{\alpha_{iA} - \varphi}$$

$$R_{min} + 1 = \frac{1 \times 0.33}{0.33 - 2.0447} + \frac{4.4035 \times 0.85}{4.4035 - 2.0447} \frac{12.4125 \times 0.12}{12.4125 - 2.0447}$$

$R_{min} + 1 = 10.6$

$R_{min} = 9.6$

Thus,

$R = 1.5\ R_{min}$

R = 1.5 × 9.6

R = 14.4

Using Gilliland Equation, we get,

$$\underline{X} = \frac{R - R_{min}}{R+1}$$

$$\underline{X} = \frac{14.4 - 9.6}{14.4 + 1}$$

$\underline{X}$ = 0.3117

$$\underline{Y} = 1 + e^{\frac{(1+54.5\,X)(X-1)}{(11+117.2\,X)(\sqrt{X})}}$$

$$\underline{Y} = 1 + e^{\frac{[1+(54.5 \times 0.3117)](0.3117 - 1)}{[11+(117.2 \times 0.3117)]\,(\sqrt{0.3117})}}$$

$\underline{Y}$ = 0.7728

Thus,

$$\underline{Y} = \frac{N - N_{min}}{N + 1}$$

$$0.7728 = \frac{N - 2.7234}{N+1}$$

N = 15.39 ~ 16 Stages, i.e., 15 trays and 1 reboiler

Using Kirkbride Equation, we get,

$$\frac{N_R}{N_S} = [\frac{x_{HK \cdot L}}{x_{LK \cdot L}} \times (\frac{x_{LK \cdot N}}{x_{HK \cdot M}})^2 \times \frac{N}{M}]^{0.206}$$

$$\frac{N_R}{N_S} = [\frac{033}{0.66} \times (\frac{0.33}{0.03})^2 \times (\frac{252.5499}{96.0766})]^{0 \cdot 206}$$

$$\frac{N_R}{N_S} = 2.84$$

But,

$N = N_R + N_S = 16$

$16 = N_S + 2.84\ N_S$

$N_S = 4.17$ Stages ~ 4 Stages

$N_R = 16 – 4.17 = 11.83$ ~ 12 Stages

Thus, feed is added on the 13th Tray from the top.

8.1.4 Tower Diameter and Height Calculation

Distillate for Stream M, D = 96.0766 kg/h

Bottom Product for Steam N, W = 252.5499 kg/h

At the top of the tower at 106°C,

Vapor Flow rate, Stream V = 240.1915 kg/h

Liquid Flow rate, Stream L = 144.1149 kg/h

Average Molecular mass of stream V

$= 0.03 \times 96.08 + 0.85 \times 18 + 0.12 \times 46.46$

=23.81 kg/kmol

Molar flow rate for stream V,

$$n = \frac{240.1915}{23.81}$$

n = 10.09 kmol/h

From ideal gas law,

PV = nRT

Volume = $\frac{(10.09\times0.082058\times379.15)}{1}$

Volume = 313.70 m^3/h

Volume flow rate for stream V = 313.70 m^3/h

Volume flow rate for stream V = 11078.211 ft^3/h

Vapor density, $\rho_G = \frac{240.1915}{313.70}$

ρ_G = 0.766 kg/m^3

Liquid density for stream L

$\frac{1}{\rho_L} = \frac{m_{Furfural}}{\rho_{Furfural}} + \frac{m_{Water}}{\rho_{Water}} + \frac{m_{CDP}}{\rho_{CDP}}$

$\frac{1}{\rho_L} = \frac{0.13}{1160} + \frac{0.64}{997} + \frac{0.23}{789}$

ρ_L = 995.417 kg/m^3

Using Fair Method, the flow parameter,

$F_{lv} = (\frac{L}{V})(\frac{\rho_L}{\rho_G})^{0.5}$

$F_{lv} = (\frac{144.1149}{240.1915})(\frac{0.766}{955.417})^{0.5}$

F_{lv} = 0.017

Assuming Tray Spacing,

S = 18 inch

S= 0.4572 m

From Lygeros and Magoulas equation for Sounders- Brown flooding constant,

$C_{SB} = 0.03445 + 5.421 \times 10^{-3} \times S^{0.755}\, e^{(-1.463 \times F_{lv}^{\,0.842})}$

$C_{SB} = 0.03445 + 5.421 \times 10^{-3} \times (18)^{0.755}\, e^{(-1.463 \times 0.017^{\,0.842})}$

$C_{SB} = 0.08$ ft/s

Flooding velocity, $u_{fl} = C_{SB}\,[\frac{\rho_L}{\rho_G} - 1]^{0.5}$

$u_{fl} = 0.08\,[\frac{955.417-0.766}{0.766}]^{0.5}$

$u_{fl} = 2.83$ ft/s

Taking operating velocity 50% of flooding velocity,

$u_s = 0.5 \times 2.83$

$u_s = 1.415$ ft/s

Fractional approach, $f_{fl} = 0.6$

For sieve tray, fractional downcomer area, $f_d = 0.8$

Tower cross section at the top,

$$A_T = \frac{V}{(f_{fl}\, u_s)(1 - f_d)}$$

$$A_T = \frac{11078.211}{3600 \times (0.6 \times 1.1415) \times (1 - .8)}$$

$A_T = 22.4652\ ft^2$

Tower Top Diameter,

D = $\sqrt{\frac{4 \times A_T}{\pi}}$

D = $\sqrt{\frac{4 \times 22.4625}{\pi}}$

D = 5.3482 ft

D = 1.63 m

At the bottom of the tower at 132 °C,

Vapor Flow rate, Stream $\overline{V}$ = 588. 8182 kg/h

Liquid Flow rate, Stream $\overline{L}$ = 841.3681 kg/h

Average Molecular mass of stream $\overline{V}$

= 0.66 × 96.08 + 0.33 × 18 + 0.07 × 46.46

= 65.64 kg/kmol

Molar flow rate for stream $\overline{V}$,

n = $\frac{588.8182}{65.64}$

n = 8.9704 kmol/h

From ideal gas law, PV = nRT

Volume = $\frac{8.9704 \times 0.082 \times 405.15}{1}$

Volume = 298.047 m^3/h

Volume flow rate for stream $\overline{V}$ = 298.047 m^3/h = 10525.43047 ft^3/h

Vapor density, ρ_G = 588.8182/298.047

$\rho_G = 1.97\ \mathrm{kg/m^3}$

Liquid density for stream $\bar{L}$

$1/\rho_L = (m_{furfural}/\rho_{furfural}) + (m_{water}/\rho_{water}) + (m_{CDP}/\rho_{CDP})$

$1/\rho_L = (0.91/1160) + (0.086/997) + (0.004/789)$

$\rho_L = 1141.798\ \mathrm{kg/m^3}$

Using Fair Method, the flow parameter,

$$F_{lv} = \left(\frac{\bar{L}}{\bar{Y}}\right)\sqrt{\frac{\rho_G}{\rho_L}}$$

$$F_{lv} = \left(\frac{841.3681}{588.8182}\right)\sqrt{\frac{1.97}{1141.798}}$$

$F_{lv} = 0.0593$

Assuming Tray Spacing,

S = 18 inch

S = 0.4572 m

From Lygeros and Magoulas equation for Sounders- Brown flooding constant,

$$C_{SB} = 0.03445 + 5.421 \times 10^{-3}\, S^{0.755}\, e^{-1.463\, F_{lv}^{\ 0.842}}$$

$$C_{SB} = 0.03445 + 5.421 \times 10^{-3}\,(18)^{0.755}\, e^{-1.463 \times 0.0593^{0.842}}$$

$C_{SB} = 0.076$ ft/s

Flooding velocity, $u_{fl} = C_{SB}\,\frac{(\rho_L - \rho_G)^{0.5}}{\rho_G}$

$$u_{fl} = 0.076 \times \frac{(1141.798 - 1.97)^{0.5}}{1.97}$$

$$u_{fl} = 1.8281 \text{ ft/s}$$

Taking operating velocity 50% of flooding velocity,

$u_s = 0.5 \times 1.8281$

$u_s = 0.914$ ft/s

Fractional approach, $f_{fl} = 0.6$

For sieve tray, fractional downcomer area, $f_d = 0.8$

Tower cross section at the bottom,

$$A_T = \frac{V}{(f_{fl}\, u_s)(1 - f_d)}$$

$$A_T = A_T = \frac{10525.43047}{3600 \times (0.6 \times 0.914) \times (1 - .8)}$$

$A_T = 26.6569$ ft^2

Tower bottom Diameter,

$$D = \sqrt{\frac{4 \times A_T}{\pi}}$$

$$D = \sqrt{\frac{4 \times 26.6569}{\pi}}$$

D = 5.8258 ft

D = 1.7757 m

Column Height = Actual No. of Trays × Tray spacing + 2 × Tray Spacing

(Ref: https://www.researchgate.net/publication/315733185)

Column Height = 18 + (16-1) × 18 + 18 = 306 inch = 7.7724 m

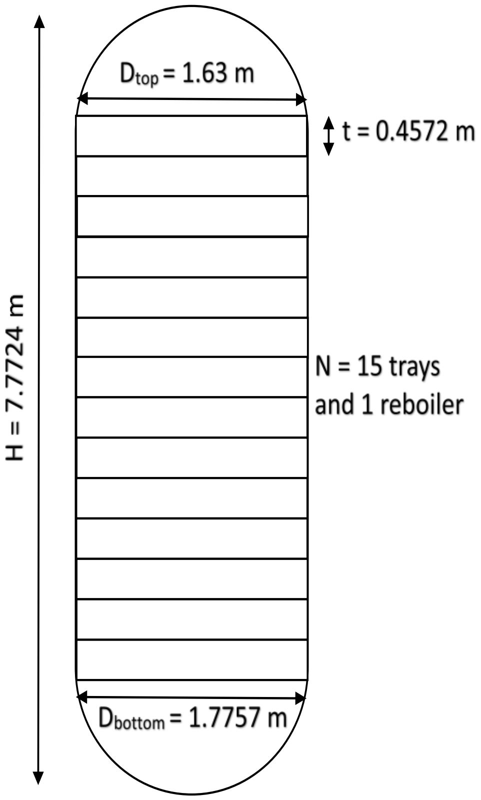

Fig 8.1 : Distillation Column design

8.2 DESIGN OF STORAGE TANK

Data:

1. Density of furfural, $\rho_{Furfural}$ = 1160 kg/m^3 [19]
2. Density of water, ρ_{Water} = 997 kg/m^3 [18]
3. Density of CDP, ρ_{CDP} = 789 kg/m^3 [19]

Assumptions:

1. The annual per unit cost of fabrication of the tank per unit area is 1.75 times the annual cost of fabrication of bottom per unit area, i.e., $C_1 = 1.75\ C_2$.

2. The annual cost of fabricated roof per unit area is 0.8 times the annual cost of fabrication of bottom per unit area, i.e., $C_3 = 0.8\ C_2$.
3. The annual cost of foundation and land taken together per unit area of the tank bottom is 0.14 times the annual cost of fabrication per unit area, i.e., $C_4 + C_5 = 0.14\ C_2$.

Where,

C_1 = Annual cost of fabricated shell per unit area in Rs/ft^2.

C_2 = Annual cost of fabricated bottom per unit area in Rs/ft^2.

C_3 = Annual cost of fabricated roof per unit area in Rs/ft^2.

C_4 = Annual cost of installation of foundation under the vessel in Rs/ft^2.

C_5 = Annual cost of land under the tank chargeable to the tank in Rs/ft^2 of tank bottom area.

C = Total annual cost of tank in Rs/ft^2.

Density of product stream N,

$$\frac{1}{\rho_N} = \frac{m_{Furfural}}{\rho_{Furfural}} + \frac{m_{Water}}{\rho_{Water}} + \frac{m_{CDP}}{\rho_{CDP}}$$

$$\frac{1}{\rho_N} = \frac{0.91}{1160} + \frac{0.086}{997} + \frac{0.004}{789}$$

$\rho_N = 1141.798\ kg/m^3$

Mass flow rate of product stream, N = 252.5499 kg/h

Volume flow rate of product stream, N = $252.5499/\rho_N$

$$\text{Volume} = \frac{252.5499}{1141.798}$$

Volume = 0.2212 m^3/h

Considering storage capacity for 6 months (30 days in each month), we get, Volume of the storage tank = $0.2212 \times 24 \times 30 \times 6 = 955.584\ m^3$

Considering 25% excess volume, we get,

Design volume of the storage tank,

$V = 1.25 \times 955.584 = 1194.48\ m^3$

<u>Trial 1</u>:

Assuming the tank to be a small tank

Optimum tank proportion,

$$\frac{D}{H} = \frac{2 \times C_1}{C_2 + C_3 + C_4 + C_5}$$

$$\frac{D}{H} = \frac{2 \times 1.75\ C_2}{C_2 + (0.8 \times C_2) + (0.14 \times C_2)}$$

$$\frac{D}{H} = 1.8$$

Therefore, $D = 1.8\ H$

Now, $V = \frac{\pi\ D^2 H}{4}$

$1194.48 = \frac{\pi \times 1.6\ H^2 \times H}{4}$

$H = 9.4537\ m = 31.016\ ft$

So, $D = 1.8 \times 9.4537$

$D = 17.017\ m = 55.83\ ft$

Assuming, double welded butt joint, condition for small tank is $D\ (H-1) \leq 1720$

$D\ (H-1) = 55.83\ (31.016 - 1) = 1675.79 < 1720$

Thus, our assumption of considering a small tank is correct.

Optimum tank proportion, $\frac{D}{H}$ = 1.8

Now, circumference of the tank = $\pi D = \pi \times 17.017 = 53.4605$ m

Assuming ‘n’ to be the number of plates. The total gap allowance for double welded butt joint is given by $2n \times 10^{-3}$ m.

Effective circumference of the tank = $\pi D - (2n \times 10^{-3})$

Length of each plate, $L = \frac{\pi D - (2n \times 10^{-3})}{n}$

For n = 7,

$$L = \frac{53.4605 - (2 \times 7 \times 10^{-3})}{7}$$

L = 7.63 m

Width of the plate = $\frac{H}{n} = \frac{9.537}{7}$

$\frac{H}{n}$ = 1.3505 m = 1350.5 mm

Standard width available is W = 1.5 m nearest to 1.3505 m [23]

According to Indian Standards, number of plates are equal to the number of thickness sections for storage tank design. Thus, number of thickness sections, n = 7.

Considering IS: 2002 -1962, Steel 2B as material of construction at 200 °F.

Shear stress value is S = 1.18 kg_f/mm^2 =1180 kg_f/cm^2. [24]

Corrosion allowance t_c = 0.3 mm

Joint efficiency for double welded butt joint, E = 0.85

Specific gravity, $g = \frac{\rho_N}{\rho_{water}}$

$g = \frac{1141.798}{997}$

$g = 1.14$

From IS: 803-1976 code book of Indian Standards, Clause 6.3.3/6.3.3.1, Plate Thickness, t given by

Plate thickness, $t = \frac{50\ (H - 0.3) \times D \times G}{S \times E}$;   if S is in kg_f/cm^2. [25]

Thickness of 1st section, t_1

$t_1 = \frac{50\ (9.4537\ - 0.3) \times 17.017\ \times 1.14}{1180 \times 0.85}$

$t_1 = 8.85$ mm

Adding corrosion allowance = 8.85 + 0.3 = 9.15 mm

Thickness of 2nd section t_2

$t_2 = \frac{50\ (7.9537\ - 0.3) \times 17.017\ \times 1.14}{1180 \times 0.85}$

$t_2 = 7.40$ mm

Adding corrosion allowance = 7.40 + 0.3 = 7.70 mm

Thickness of 3rd section t_3

$t_3 = \frac{50\ (6.4537\ - 0.3) \times 17.017\ \times 1.14}{1180 \times 0.85}$

$t_3 = 5.95$ mm

Adding corrosion allowance = 6.25 + 0.3 = 6.25 mm

Thickness of 4th section t_4

$$t_4 = \frac{50\ (4.9537\ -0.3) \times 17.017\ \times 1.14}{1180 \times 0.85}$$

t_4 = 4.5 mm

Adding corrosion allowance = 4.5 + 0.3 = 4.80 mm

According to Clause 6.3.3.2, IS: 803-1976 code book of Indian Standards, minimum thickness for tank diameter, D = 17.017 m is 6 mm.

So, the thickness of the sections, $t_4 = t_5 = t_6 = t_7$ = 6 mm

Table 8.9: Summary table for thickness sections

Thickness section, n	**Height, H(m)**	**Thickness without corrosion allowance, t (mm)**	**Thickness with corrosion allowance, t + t_c (mm)**	**Standard Thickness (mm)**
1	9.4537	8.85	9.15	10
2	7.9537	7.40	7.70	8
3	6.4537	5.95	6.25	7
4	4.9537	4.50	4.80	6
5	-	-	-	6
6	-	-	-	6
7	-	-	-	6

(For standard thickness values Ref: B.C. Bhattacharyya Book, Table B-1, Appendix B, Page 269)

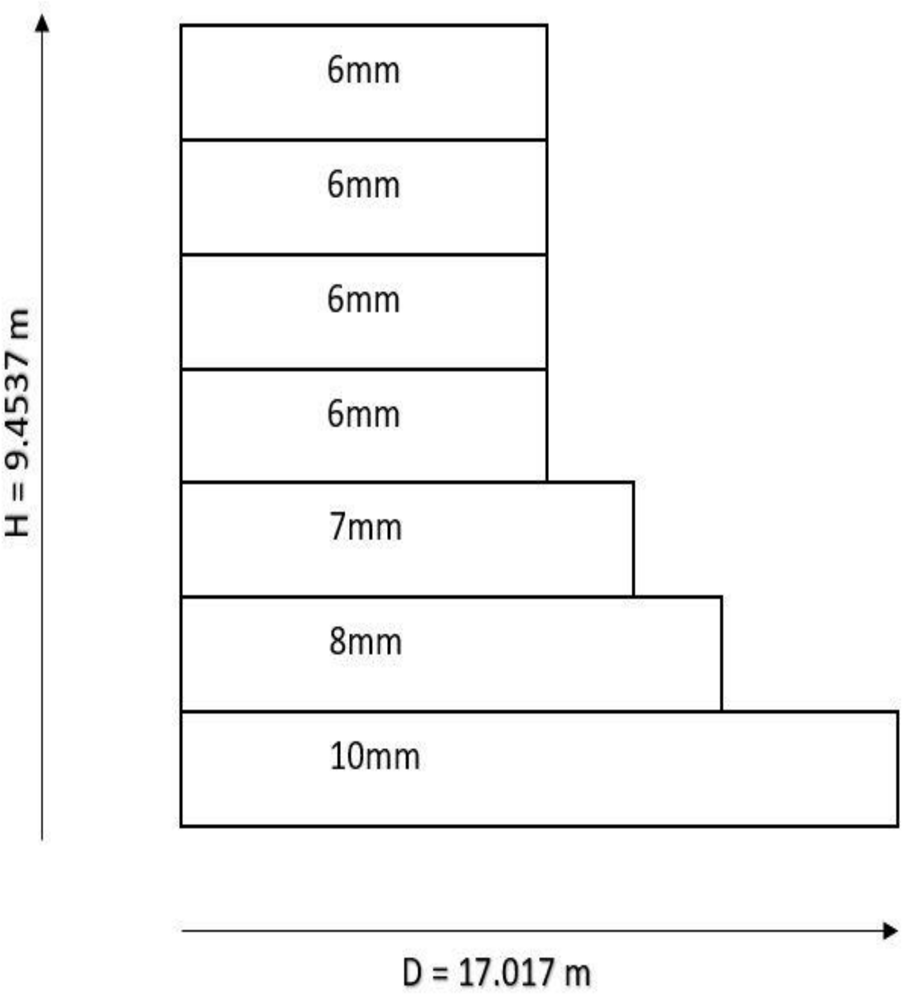

Fig. 8.2 Thickness sections of storage tank.

CONCLUSION

Furfural being a very important non-petroleum derived chemical, has a widespread application ranging from its direct usage to synthesis of other important chemicals. India being a country of wide agricultural activities, availability of raw materials for the production process which is biomass like bagasse or rice hulls will not be a matter of concern. Although procuring hardwood may become challenging, but its usage is not essential and can be compensated by other sources of biomass. The production processes suggests that the residence time for hydrolysis reaction in a Plug flow reactor varies from 60 to 120 seconds with a percentage yield of 40 to 60 percent of the biomass taken as feed. Sulphuric acid being the catalyst used varies in concentration ranging from 0.8 to 5% wt. /wt. and the optimum reaction temperature of 170 to 250°C. Although much higher temperature is not suggested as it may result in degradation and charring of the organic thermo labile raw material. Sodium hydroxide is the suggested neutralising agent for sulphuric acid catalyst, although other agents like Potassium bases and other Sodium bases may also be used for this purpose. Product purity ranging from 85 to 95% can be obtained with one distillation column in the production system. More number of distillation columns can be added if higher purity is expected. The waste generated from the production process contains organic matter rich in nutrients and can be used as a fertiliser in agricultural activities after proper processing. Future works may include studies of other raw materials and also the reacting conditions so that higher percentage yields can be obtained.

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