TREATMENT OF FLUORIDE CONTAMINATED GROUND WATER USING ADSORPTION TECHNIQUE

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ABSTRACT

The presence of excessive fluoride in groundwater is a widespread issue that poses a significant health risk to populations worldwide. In this report, the effectiveness of various adsorbents for the removal of fluoride from groundwater has been investigated. Adsorption is a promising technique due to its simplicity, cost-effectiveness, and ability to selectively target fluoride ions.

The report begins with a comprehensive overview of the sources, health effects and fluoride toxicity, and conventional methods of fluoride removal in groundwater. The review of literature explores existing methods employed for fluoride removal, highlighting the advantages and limitations of each technique. Adsorption emerges as a viable solution due to its high efficiency and low maintenance requirements.

Five different types of adsorbents which are Elephant Apple Leaf Powder (ELP), Elephant Apple Bark Powder (EBP), Elephant Apple Fruit Powder (EFP), Carbonized Elephant Apple Leaf Powder (CELP) and Carbonized Elephant Apple Leaf Powder impregnated with H_3PO_4 (CELP-H_3PO_4) have been prepared to determine their fluoride adsorption potential and the commercially available activated charcoal (CAC) has also been used as the adsorbent for comparing the fluoride removal capacity of the prepared adsorbents. Batch adsorption studies were carried out and for the initial fluoride concentration of 5 ppm, adsorbent dosage of 2 g/L, operating temperature of 25 °C, a constant rate of stirring and optimal contact time, the maximum fluoride removal for ELP was 6.16%, for EBP it was 4.26%, for EFP it was 5.05%, for CELP it was 6.12%, for CELP-H_3PO_4 it was 32.71% and for CAC it was 7.49%. The initial fluoride content for the testing of CELP-H_3PO_4 was varied and for the initial fluoride concentration of 3 ppm, the maximum fluoride removal of 50.61% was obtained for the optimal conditions.

Overall, this report provides valuable insights into the removal of fluoride from groundwater using adsorbents. The findings highlight the effectiveness of adsorption as a viable method for fluoride removal, thereby offering a promising solution to mitigate the health risks associated with excessive fluoride concentrations in groundwater.

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CHAPTER 1

INTRODUCTION

1.1. WATER AND ITS IMPACT

Water is the most abundant substance in living systems, making up 70% or more of the weight of most organism. The appearance of first living organisms on earth is without a doubt to be in an aqueous environment and the course of evolution has been shaped by the properties of the aqueous medium in which life began. The structure, self-assembly properties of all cellular components are influenced by the water molecules and its ionization product H^+ and OH^-.

Water is the only natural substance that's found in all three states – solid, liquid and gas. The cohesive forces that make water a liquid at room temperature are provided by hydrogen bonds between water molecules. This also favors the extreme ordering of molecules that's crystalline water (ice). The unstable electron sharing of two electric dipoles in the water patch, one along each of the H-O bonds, the sum of the two partial positive charges is equal in magnitude to oxygen atoms which bears a partial negative charge, each hydrogen atoms which bears a partial positive charge. As a result, electrostatic attraction between oxygen atom of one water molecule and hydrogen of another forms the hydrogen bond. Water readily dissolves most of the biomolecules as it is a polar solvent. Water is considered to be a neutral result with a pH value of 7. result having pH lesser than 7 are alkaline or introductory, the attention of OH^- is lesser than that of H^+ and result with pH value lower than 7 is considered to be acidic.

Water is critical component for socio-profitable development, healthy ecosystem, energy and food product and for mortal race survival. It is also the core of sustainable development. Although according to UNICEF and WHO report in 2019, 2.2 billion people warrant access to safely managed drinking water service.

Ground water impurity is an enormous problem. Studies shows the presence of unhealthy amounts of fluoride present in groundwater in India. Estimation shows that waterborne complaint has an economic burden of roughly USD 600 million a year in India.

1.2. FLUORIDE IN OUR ENVIRONMENT

Fluorine is the first member of halogen family. It is a pale yellow-greenish, irritating diatomic gas. Fluorine is the 13th most abundant element in the earth's crust and occurs naturally.

Parameters	**Values**
Atomic Number	9
Atomic Mass	18.998 g/mol
Boiling Point	-188 °C
Melting Point	-219 °C
Density	1.8×10^{-3} g/cm^3 at 20 °C
Electronegativity	4
Van der Waal radius	0.136 nm
Ionic Radius	0.136 nm
Isotopes	2
Electronic Shell	[He] $2s^2 2p^5$
First Ionization	1680.6 kJ/mol
Standard Potential	-2.87 V

Table 1.1: *Chemical properties of fluorine*

Fluorine is the most electronegative of all the elements and hence it is so chemically reactive that it rarely occurs naturally in the elemental state. Because of this, fluorine in the environment is found in combined state as fluorides, the ionic form of fluorine. Fluorine readily reacts with most organic and inorganic substances; with metals it gives fluoride. In general, fluoride is always associated with metals in solid state. In aqueous solution, fluoride can be found as either free ions or combined to other metals and metalloids in complex forms and with water it readily forms hydrofluoric acid at lower pH (<5.0).

Fluoride is found in all the natural water bodies at various concentrations. In water, fluoride associate with various constituent present in it, particularly with aluminium in freshwater, calcium and magnesium in seawater, and also found with the sediment particles.

Seawater typically contains about 1.0 mg/L of fluoride, while rivers and lakes generally exhibit concentrations less than 0.5 mg/L. In well, fluoride generally range from 0.02-1.5 mg/L, but exceed 1.5 mg/L in some parts of the world. The fluoride containing minerals in rocks and soil are the main cause of high fluoride content in ground water, which is primary source of drinking water in many parts of the world.

1.3. HEALTH EFFECTS AND FLUORIDE TOXICITY

Fluoride has been considered as an essential micro-nutrient in human body and fluoride in drinking water may be beneficial for human body depending on its concentration. A small amount of fluoride is essential for production and maintenance of healthy bone and teeth. Fluoride in lower concentration (<1.5 mg/L) prevents tooth decay by improving the acid resistance of dental enamel. However, fluoride also has harmful effects if consumed in excessive amount.

1.3.1. DENTAL FLUOROSIS

Dental fluorosis, also known as mottling of tooth enamel, is considered as the first adverse effect which is caused by excessive fluoride in drinking water. A fluoride content of 0.7 ppm is considered best for dental health. However, a concentration that is above 4.0 ppm could be hazardous. During childhood when teeth are developing, an exposure of high concentrations of fluoride can result in mild dental fluorosis. There will be tiny white streaks or specks in the enamel of the tooth. This can result in discoloration of the teeth. In more severe cases, the teeth may have brown strains and rough, pitted enamel that is difficult to clean.

1.3.2. SKELETAL FLUOROSIS

A bone disease known as skeletal fluorosis can occur if exposed to excess of fluoride. This can result in pain and damage to bones and joints over the period of time. Chronic intake of drinking water with elevated levels of fluoride can have serious effect on skeletal tissues. This may cause the bones to become hardened and less elastic which would increase the risk of fractures. If the bones thicken and bone tissue accumulates then it can contribute to impaired joint mobility. Pain in bones and joints, muscle weakness, stiffness of joints and chronic fatigue are the signs of early stages of skeletal fluorosis. During later stages, calcification of the bones takes place and symptoms of osteosclerosis are observed, in which the bones become denser with development of abnormal crystalline structure. In the advance stage, the bones and joint become completely weak and finally the patient is left crippled. Crippling skeletal fluorosis may develop due to intake of water that contains 10.0 mg/L fluoride over a prolonged period of time.

1.3.3. THYROID PROBLEMS

Hyperparathyroidism can occur when the parathyroid gland is damaged due to excess of fluoride. This involves uncontrolled secretion of parathyroid hormones. This can result in higher-than-normal concentrations of calcium in the blood and depletion of calcium in bone structure.

1.4. FLUORIDE AND OTHER INORGANIC CONSTITUENTS IN GROUNDWATER OF GUWAHATI, ASSAM

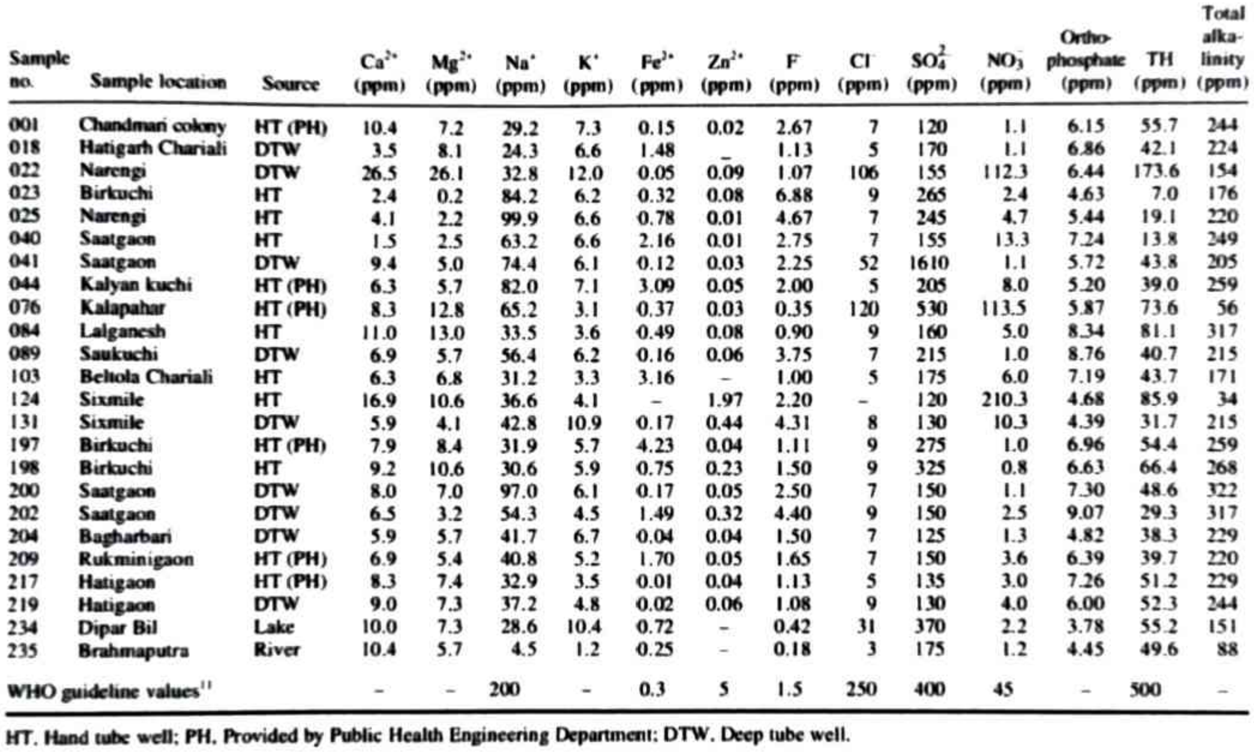
The distribution of fluoride in groundwater is shown in Fig 1.1.

Source: https://www.researchgate.net/figure/Map-showing-the-distribution-of-fluoride-in-Guwahati-Location-of-fluoride-affected_fig1_239929511

***Fig 1.1:** Map showing the distribution of fluoride in the ground water of Guwahati*

The south-eastern plains of the city have been found to possess high fluoride concentration. The highest fluoride concentration has been found in eastern part of the south-eastern plains, as shown in Fig 1.1.

The area has a narrow link with the Brahmaputra in the north-eastern corner of the city and a relatively wider opening towards Dipor Bil and the Brahmaputra. In this area, the fluoride concentration of the groundwater gradually decreases from the east towards the west. The groundwater samples of the western part of Guwahati are mostly deficient in fluoride content. This indicates that the source of fluoride is present in the eastern part of the south-eastern plains. In the western part of the city, the fluoride concentration in the groundwater has been found to be 0.18 ppm. Table 1.2 shows the concentration of various ions and other parameters of some selected samples most of which possess high concentration of fluoride.



Sample no.	Sample location	Source	Ca^{2+} (ppm)	Mg^{2+} (ppm)	Na^{+} (ppm)	K^{+} (ppm)	Fe^{2+} (ppm)	Zn^{2+} (ppm)	F^{-} (ppm)	Cl^{-} (ppm)	SO_4^{2-} (ppm)	NO_3^{-} (ppm)	Ortho-phosphate (ppm)	TH (ppm)	Total alka-linity (ppm)
001	Chandmari colony	HT (PH)	10.4	7.2	29.2	7.3	0.15	0.02	2.67	7	120	1.1	6.15	55.7	244
018	Hatigarh Chariali	DTW	3.5	8.1	24.3	6.6	1.48	–	1.13	5	170	1.1	6.86	42.1	224
022	Narengi	DTW	26.5	26.1	32.8	12.0	0.05	0.09	1.07	106	155	112.3	6.44	173.6	154
023	Birkuchi	HT	2.4	0.2	84.2	6.2	0.32	0.08	6.88	9	265	2.4	4.63	7.0	176
025	Narengi	HT	4.1	2.2	99.9	6.6	0.78	0.01	4.67	7	245	4.7	5.44	19.1	220
040	Saatgaon	HT	1.5	2.5	63.2	6.6	2.16	0.01	2.75	7	155	13.3	7.24	13.8	249
041	Saatgaon	DTW	9.4	5.0	74.4	6.1	0.12	0.03	2.25	52	1610	1.1	5.72	43.8	205
044	Kalyan kuchi	HT (PH)	6.3	5.7	82.0	7.1	3.09	0.05	2.00	5	205	8.0	5.20	39.0	259
076	Kalapahar	HT (PH)	8.3	12.8	65.2	3.1	0.37	0.03	0.35	120	530	113.5	5.87	73.6	56
084	Lalganesh	HT	11.0	13.0	33.5	3.6	0.49	0.08	0.90	9	160	5.0	8.34	81.1	317
089	Saukuchi	DTW	6.9	5.7	56.4	6.2	0.16	0.06	3.75	7	215	1.0	8.76	40.7	215
103	Beltola Chariali	HT	6.3	6.8	31.2	3.3	3.16	–	1.00	5	175	6.0	7.19	43.7	171
124	Sixmile	HT	16.9	10.6	36.6	4.1	–	1.97	2.20	–	120	210.3	4.68	85.9	34
131	Sixmile	DTW	5.9	4.1	42.8	10.9	0.17	0.44	4.31	8	130	10.3	4.39	31.7	215
197	Birkuchi	HT (PH)	7.9	8.4	31.9	5.7	4.23	0.04	1.11	9	275	1.0	6.96	54.4	259
198	Birkuchi	HT	9.2	10.6	30.6	5.9	0.75	0.23	1.50	9	325	0.8	6.63	66.4	268
200	Saatgaon	DTW	8.0	7.0	97.0	6.1	0.17	0.05	2.50	7	150	1.1	7.30	48.6	322
202	Saatgaon	DTW	6.5	3.2	54.3	4.5	1.49	0.32	4.40	9	150	2.5	9.07	29.3	317
204	Bagharbari	DTW	5.9	5.7	41.7	6.7	0.04	0.04	1.50	7	125	1.3	4.82	38.3	229
209	Rukminigaon	HT (PH)	6.9	5.4	40.8	5.2	1.70	0.05	1.65	7	150	3.6	6.39	39.7	220
217	Hatigaon	HT (PH)	8.3	7.4	32.9	3.5	0.01	0.04	1.13	5	135	3.0	7.26	51.2	229
219	Hatigaon	DTW	9.0	7.3	37.2	4.8	0.02	0.06	1.08	9	130	4.0	6.00	52.3	244
234	Dipar Bil	Lake	10.0	7.3	28.6	10.4	0.72	–	0.42	31	370	2.2	3.78	55.2	151
235	Brahmaputra	River	10.4	5.7	4.5	1.2	0.25	–	0.18	3	175	1.2	4.45	49.6	88
WHO guideline values[11]			–	–	200	–	0.3	5	1.5	250	400	45	–	500	–

HT. Hand tube well; PH. Provided by Public Health Engineering Department; DTW. Deep tube well.

Source: https://www.researchgate.net/figure/Results-of-analysis-of-selected-groundwater-samples-in-Guwahati-city_tbl1_239929511

***Table 1.2:** Concentration of the ions in the ground water at the various locations of Guwahati*

Area	Location	Total number of samples	Percentage of samples in different ranges of fluoride content (ppm)			
			0.1–0.6	0.6–1.5	1.5–3.0	>3.0
Entire city	–	235	45.5	43.8	6.0	4.7
Southeast plains	Bonda, Birkuchi, Narengi, Chandmari, Mathgharia, Noonmati, Saatgaon, Hengerabari, Sixmile, Boidangbori, Khanapara, Beltola, Hatigaon, Bashishta, Saukuchi, Lokhra Chariali	127	27.5	52.8	11.0	8.7
Eastern part of southeast plains	Bonda, Birkuchi, Narengi, Chandmari, Saatgaon, Hengerabari, Sixmile, Panjabari	71	28.2	39.4	18.3	14.1

Source: https://www.jstor.org/stable/24109107

Table 1.3: *Distribution of fluoride in groundwater in different areas of Guwahati*

Table 1.3 shows us the 235 samples out of which 10.7% were found to have a fluoride concentration above 1.5ppm, the guideline value of WHO, and 45.5% of those samples are below 0.6 ppm in fluoride.

1.5. CONVENTIONAL METHODS OF FLUORIDE REMOVAL

These are the commonly applied techniques for fluoride removal from drinking water –

- Ion Exchange
- Membrane Separation
- Precipitation
- Coagulation
- Adsorption

1.6. SELECTION OF DEFLUORIDATION METHOD

The selection of the method for defluoridation of water can be done after comparing the different techniques of fluoride removal. Each technique has its own advantages and disadvantages and the technique which fulfils the various criteria like being low cost, easy to use etc. would be selected as the technique for fluoride removal.

1.6.1. ION EXCHANGE

In this method of defluoridation, the problem is the price of resin, its regeneration, resultant waste disposal requirements, and it isn't selective enough. This makes this method inefficient and expensive.

1.6.2. MEMBRANE SEPARATION

In this method of defluoridation, the problem is the elevated cost of membrane acquisition, operation and the disposal of concentrates, which makes the post treatment of water necessary, making the process expensive.

1.6.3. PRECIPITATION

In this method of defluoridation, the problem is that lime-based processes include low solubility of the resulting calcium hydroxide, which hinders the adequate removal of fluoride from the water.

1.6.4. COAGULATION

In this method of defluoridation, the problem is that although economical but it requires high doses, this leads to high residual concentrations and hence produces significant amount of sludge.

1.6.5. ADSORPTION

In this method of defluoridation, the technique is very promising due to its handy operation, low-cost operation, increased selectivity and readiness of adsorbents.

Hence, this project utilises the use of adsorption technique as a method of de-fluoridation.

1.7. AIMS AND OBJECTIVES

The aims and objectives of the project work are as follows –

- To study the various adsorption techniques for fluoride removal from ground water.
- To prepare low-cost, eco-friendly adsorbents for fluoride removal.
- To check the fluoride removal capacity of the adsorbents.

CHAPTER 2

LITERATURE REVIEW

2.1 ADSORBENTS FOR FLUORIDE REMOVAL

The removal of fluoride from water is easily carried out using adsorption technique and it also has a lot of advantages over the other water purification method. Various adsorbents have been studied and worked upon till now for this purpose. In the study conducted by Zúñiga-muro et al. (2017), bone char was modified with cerium [27] and used for fluoride adsorption purpose. In the study carried out by Wong and Stenstrom (2018) calcium carbonate [26] directly purchased from market was used for fluoride adsorption studies. In the study conducted by Borgohain et al. (2020) porous MgO nanostructures [5] were synthesized through sol-gel and hydrothermal methods to be used as adsorbents for fluoride removal. Gidi et al. (2019), prepared the novel clay composite composed of clay, grog, bone char and saw dust [12] that were mixed in a definite proportion to be used as an adsorbent for the removal of fluoride from ground water. Maliyekkal et al. (2006) prepared manganese oxide coated alumina [17] to test for its fluoride removal capacity. Mukherjee et al. (2017) had conducted the study on algal biomass treated with Ca^{+2} [20] for the removal of fluoride from water and wastewater by adsorption process. In the study conducted by S Kumar et al. (2008), fluoride removal was studied by the thermally activated carbon prepared from Neem (*Azadirachta indica*) and Kikar (*Acacia arabica*) leaves. In the study reported by Roy et al. (2017), activated charcoal impregnated with calcium was used for fluoride adsorption. NA Medellin-Castillo et al. (2007), used bone char [18] for his study as the adsorbent for fluoride removal. The adsorption efficiency depends on a number of factors. The bio-adsorbents that are easy to procure like orange peel, banana peel etc. have shown good adsorption capacity and fluoride removal efficiency. The various bioadsorbents that have been used for fluoride removal are mentioned below.

2.2. BIOSORPTION USING NEEM LEAF POWDER

In this study conducted by Bharali et al. (2015), adsorption using neem leaf powder (NLP) for fluoride removal [2] was carried out. The adsorbent was prepared from mature leaves of neem tree by cleaning, sun drying for 3 to 4 days and then drying in an air oven at 60 – 70 °C. After this, the dried neem leaves were crushed and grinded and was sieved to select the 74 – 105 micron fractions for the process. The specific surface area of NLP was found to be 32.94 m^2/g. The fluoride removal capacity was found to be above 80% at an effective pH range of 5.0 – 7.0 with an equilibrium time for adsorption to be at 60 minutes. The adsorption process followed second order kinetics and obeyed Freundlich, Langmuir and Temkin isotherm models.

2.3. FLUORIDE REMOVAL BY COCONUT HUSK ACTIVATED CARBON

In this study conducted by Talat et al. (2018), waste coconut husk [24] was used to prepare activated carbon for fluoride removal. The coconut husk was cleaned, dried and then carbonized at a temperature of 700°C in a purified nitrogen atmosphere for 3 hours. It was then cooled and mixed with KOH pellets in different ratios and activated to finally be used as the adsorbent. The surface area of the prepared activated carbon was found to be 1448 m^2/g by various characterization techniques. Using the adsorbent dosage at 1.4 g/L and water having fluoride concentration of 10 mg/L, the adsorption capacity was found out to be 6.5 mg/g at a pH of 5.

2.4. FLUORIDE REMOVAL BY NATURAL BANANA PEEL DUST

In this study conducted by Mondal et al. (2017), adsorption using natural banana peel (NBP) dust for fluoride removal [19] was carried out. The banana peels were washed with water to remove impurities and then dried to remove moisture. They were then cut into small pieces and then dried again at a temperature of 60°C after which they were grinded and sieved to get the particle size of 200 micron and were used as adsorbent. The optimum condition for fluoride removal was found out to be an adsorbent dosage of 0.15 g per 100 ml at a pH of 6.0 and contact time of 60 minutes. The kinetics data were found to fit with pseudo second order and Bahangam models.

2.5. FLUORIDE REMOVAL USING STEAM ACTIVATED CARBON OF WOOD APPLE SHELL

In this study conducted by Mukherjee et al. (2018), adsorption using wood apple shell [20] for fluoride removal was carried out. The shells were collected, washed and placed in an air oven for drying. The dried shells were broken in small pieces and carbonized. They were activated and then crushed and sieved through 710 micron mesh size to obtain the desired particle size for adsorption. Having an adsorbent dosage of 6 g/L, pH 5, temperature 313.15 K and initial fluoride concentration of 8 mg/L gave a maximum defluoridation of 89%. The adsorption phenomenon obeyed pseudo second order kinetics.

2.6. FLUORIDE REMOVAL USING TEA WASTE LOADED WITH AL/FE OXIDES

The tea waste loaded with Al/Fe oxides [6] were tested as an adsorbent for its fluoride removal capacity in this study conducted by Cai et al. (2015). The dried tea waste was treated with sulphuric acid solution to remove the colored and soluble components. It was then washed, dried, grounded and then sieved through mesh 60 to get the base bioadsorbent. This base adsorbent was then treated with ferric chloride and aluminum nitrate to obtain the required tea waste adsorbent loaded with Al/Fe oxides. The maximum fluoride adsorption capacities of the original tea waste, Tea-Fe, Tea-Al and Tea-Al-Fe bioadsorbents were 3.83, 10.47, 13.79 and 18.52 mg/g respectively. Using adsorbent dosage of 2 g/L, the fluoride content in the water could be reduced to less than 1.5 mg/L from an initial concentration of 10 mg/L.

2.7. FLUORIDE REMOVAL USING CHEMICALLY REDUCED TEA WASTE BIOCHAR

In the study conducted by Roy et al. (2018), chemically reduced tea waste biochar [23] had been used as the adsorbent for fluoride removal. The tea waste was dried and crushed to powder form and then placed in a tube furnace and heated at 673 K for 30 minutes. The product was cooled, grounded and sieved to obtain particles of size less than 0.2 mm. The obtained biochar was then chemically modified using Hummer's method to form carbonaceous material. This final material was then used as an adsorbent for removal of fluoride. The fluoride removal efficiency of this adsorbent under optimum condition was found to be 98.31%. The Langmuir adsorption model fitted properly under different temperatures and the adsorbent was found to follow pseudo second order kinetic model.

2.8. FLUORIDE REMOVAL USING PINEAPPLE PEEL AND ORANGE PEEL POWDERS

In this study conducted by Gandhi et al. (2016), the fluoride removal capacity and efficiency has been studied of pineapple and orange-peel powders [11]. The experiments have been carried out by batch adsorption method. The surface area of orange and pineapple peels are 36.89 cm^2 and 43.40 cm^2 respectively. The fluoride removal efficiency of orange peel powders was found to be above 90% at a pH of 6 and the efficiency of pineapple peel powders was found to be above 90% at a pH of 4. The dosage of adsorbent was taken as 0.6 g/L and contact time was of one hour for the initial fluoride concentration of 4 mg/L.

2.9. FLUORIDE REMOVAL USING POTATO PEEL AND RICE HUSK

In this study conducted by Bibi et al. (2017), the fluoride removal capacity of potato peel and rice husk [4] has been studied. Potato peel was washed and cut into small pieces and then washed again to remove the color, dust and other impurities. It was then dried and burned in a muffle furnace and the resultant ash of potato peel was grounded and sieved to get the desired particle size of less than 250 micron. Similarly, the rice husk was washed, dried, burned, grounded and sieved by the same process to obtain the required bioadsorbent. The maximum adsorption capacity was 2.91 mg/g between pH of 7 to 9. The Freundlich and Langmuir isotherm models fitted and the adsorbent was shown to follow pseudo second order kinetics.

2.10. FLUORIDE REMOVAL USING BETEL NUT COIR CHARCOAL

Betel nut coir [7] was used as the adsorbent for removal of fluoride from water in the study conducted by Chakrabarty et al. (2011). The betel nut coir was washed at first to remove the impurities and then dried. After that they were carbonized in a muffle furnace at a temperature of 200-300°C and then grinded to form powder. The charcoal powder was sieved and retained on a 400 mesh to get the desired adsorbent material. This adsorbent showed a maximum defluoridation efficiency of 92% on achieving equilibrium at the contact time of 180 minutes. Both Langmuir and Freundlich isotherm models were fitted at different temperatures and the adsorbent was shown to follow pseudo second order kinetics.

2.11. FLUORIDE REMOVAL BY THERMALLY TREATED EGG SHELLS

Egg shells [15] were taken as the base adsorbent in this study for the removal of fluoride from water in the study conducted by Lee et al. (2021). The eggshells obtained were washed and dried before use. They were then crushed and sieved to get the required particle size. After that, the samples were thermally treated in a muffle furnace at 800°C (ES-800) in a purified nitrogen atmosphere for 4 hours and then finally used as the desired adsorbent for the study. The maximum adsorption capacity of the sample was 258.28 mg/g at a pH of 7 and a temperature of 25°C. Langmuir model was found to be suitable for describing the adsorption and the adsorption was shown to follow pseudo second order kinetics.

2.12. FLUORIDE REMOVAL BY COAL MINE WASTE

In this study conducted by Department of Mining Engineering, NIT, removal of fluoride was done by using Shale [1] as an adsorbent. The defluoridization property of shale was analysed using XRD, SEM and FTIR. The maximum fluoride removal efficiency was obtained at 47.05% for contact times of 60 mins in the pH of 5-7 ranges. The absorption follows pseudo-second kinetics and Frendulich isotherm.

2.13. FLUORIDE REMOVAL BY THE THERMAL PLASMA PROCESSING OF MORINGA OLIFERA BIOCHARS

In this study, bochars were produced using different parts of Moringa oleifera [13]. The expirement was carried under Thermal plasma processing to demonstrate fluoride adsorption. Moringa Leaf were collected and processed at 1600 °C for about 3 mins in an inert atmosphere to get suitable biochars. The fluoride removed from the ground water is 85% in 18 hrs using 1 gm biochars.

2.14. FLUORIDE REMOVAL BY COMMERCIAL ACTIVATED CHARCOAL

Batch adsorption process were studied for the Commercial Activated Charcoal [25] to demonstrate the fluoride content in water. Effect on parameters like pH, dose of adsorbent, contact time and initial adsorbate concentration on fluoride removal efficiency were studied. The adsorbent dose of was taken 2.0 g/100 mL and equilibrium was achieved in 120 mins. The maximum fluoride removal was observed at 94%. For determination of kinetic constants Freudlich and Langmuir isotherms were plotted.

CHAPTER 3

MATERIALS AND METHODS

3.1. INTRODUCTION

This chapter presents the materials and methods used for the preparation of the adsorbents, chemicals used during the experimentation and the analysis of the treated water samples using the adsorbents prepared. Some of the equipment used for the preparation of the adsorbents were provided by Indian Institute of Technology, Guwahati. The analysis of the treated water samples was carried out at Pollution Control Board, Assam. The fluoride adsorption study was carried out by batch adsorption experimentations. The treated water was analyzed for the remaining amount of fluoride content.

3.2. NaF SALT

Sodium fluoride is an inorganic compound with the chemical formula NaF. It is used in trace amounts as fluoridation of drinking water, toothpaste, metallurgy and fluxes. It is a colorless or white solid that is soluble in water. It is a common source of fluoride in the manufacture of pharmaceuticals and is used to prevent tooth decay. We have used this NaF salt as a solute for preparation of synthetic fluoride solution in our project.

Chemical formula	NaF
Molar Mass	42 g/mol
Colour	Whitish
Odor	Odorless
Density	2.588 g/m^3
Melting point	993 °C
Boiling point	1704 °C

Table 3.1: *Properties of NaF salt*

Fig 3.1: NaF salt

3.3. DISTILLED WATER

Distilled water is a type of purified water. Distilled water is steam that has been boiled and cooled back to a liquid. All water, whether it comes from natural springs, wells, or regular taps, contains trace but safe levels of minerals, bacteria, pesticides, and other contaminants. Distillation removes all these impurities from the water. Also, it removes over 99.9% of minerals dissolved in water. In this project, distilled water has been used as a solvent, for cleaning all the lab apparatus and for washing all the adsorbents to remove any impurities before using the for the experimentation. The equipment used to obtain the distilled water is shown below.

Fig 3.2: Water distillation equipment

3.4. PHOSPHORIC ACID

Phosphoric acid, also known as orthophosphoric acid (H_3PO_4), is a colorless, odorless liquid with a syrupy consistency. It is a mineral acid composed of phosphorus, oxygen, and hydrogen. Phosphoric acid is widely used in various industries and has several important applications. Phosphoric acid (H_3PO_4) is commonly used in the chemical activation of lignocellulosic materials for the production of activated carbon. The chemical activation process involves impregnating the lignocellulosic material with a suitable activating agent, such as phosphoric acid, followed by carbonization. During carbonization, the phosphoric acid reacts with the carbonaceous material, promoting the formation of a highly porous structure by creating pores and increasing surface area. The use of phosphoric acid as an activating agent offers several advantages. It has a relatively low cost compared to other chemical activators like potassium hydroxide or zinc chloride. Phosphoric acid is also widely available and environmentally friendly, making it a preferred choice for many applications.

Fig 3.3: Phosphoric Acid (H_3PO_4)

3.5. MUFFLE FURNACE

A muffle furnace is a specialized piece of laboratory equipment used for high-temperature applications such as heating, calcination, and material testing. It consists of an insulated chamber, known as a muffle, which surrounds the heating element to provide uniform heat distribution and prevent contamination between the heating element and the sample. The muffle furnace is typically constructed with a robust outer casing made of materials like stainless steel or other heat-resistant alloys to withstand high temperatures. The muffle, usually made of ceramic, quartz, or other refractory materials, is located within the furnace chamber and acts as a separate heating compartment. To operate the muffle furnace, the sample or material to be heated is placed inside the muffle, ensuring it is not in direct contact with the heating element. The muffle furnace then generates heat through an electric heating element located outside the muffle. The temperature can be controlled and adjusted using a temperature controller or programmable settings. Muffle furnaces are designed to reach and maintain high temperatures, often exceeding 1000 °C.

Fig 3.4: Muffle Furnace

3.6. ORION STAR™ A214 PH/ISE METER

The Orion Star™ A214 pH/ISE Meter is a highly functional and dependable device engineered for precise pH and ion-selective electrode (ISE) measurements across various applications. Developed by a renowned analytical instrument manufacturer, Thermo Fisher Scientific, this meter offers advanced features for accurate and efficient analysis. This meter excels in measuring pH, mV (millivolts), relative mV, and ion concentration utilizing ion-selective electrodes. It covers a broad pH range, accommodating both acidic and alkaline solutions. The instrument supports multiple ion measurement modes, enabling the analysis of specific ions through ion-selective electrodes. This versatility enhances its suitability for applications in environmental analysis, pharmaceutical testing, and water quality assessment.

Fig 3.5: *Orion Star™ A214 pH/ISE Meter*

3.7. TISAB SOLUTION

TISAB II (Total Ionic Strength Adjustment Buffer II) is a reagent used in analytical chemistry, specifically in the field of ion-selective electrode (ISE) measurements. It is employed to adjust the ionic strength and pH of a sample solution, making it suitable for accurate and reliable measurements with certain types of ISEs. Ion-selective electrodes are devices that are designed to measure the concentration of specific ions in a solution. They operate based on the principle of selective ion exchange across a membrane, generating an electrical potential that is proportional to the concentration of the target ion in the sample. TISAB II serves two primary purposes in ISE measurements. First, it adjusts the ionic strength of the sample solution. This is important because variations in ionic strength can affect the potential readings of the electrode. TISAB II helps maintain a constant and known ionic strength, thereby enhancing the accuracy and precision of the measurement. Second, TISAB II helps stabilize the pH of the sample solution. It contains buffering agents that resist changes in pH, ensuring that the pH remains within a specific range optimal for the measurement. This pH stabilization is crucial because the potential response of the ion-selective electrode can be influenced by pH variations. TISAB II is typically used in conjunction with fluoride ion-selective electrodes, as fluoride is known to interfere with the measurements due to its tendency to form complexes with various metal ions present in the sample solution. The addition of TISAB II helps to complex these interfering ions, minimizing their impact on the fluoride measurement.

3.8. ELEPHANT APPLE

The elephant apple tree, known scientifically as *Dillenia indica*, is known for its unique characteristics. It is an evergreen tree native to various parts of Asia, including India, Nepal, Bangladesh, and Sri Lanka. It is native to Assam and many other Indian states and is locally known as Ou Tenga in Assam. The Elephant Apple tree reaches a height of around 15 to 25 meters. Its trunk is sturdy and covered in rough, brownish-gray bark. The tree branches out abundantly, forming a broad, rounded canopy. One of the most striking features of the Elephant Apple tree is its large, leathery leaves. These leaves are glossy green, oval-shaped, and have prominent veins running through them. They can grow up to 30 centimeters in length, creating a lush and vibrant canopy. The flowers are large, with white or cream-colored petals that surround a cluster of golden stamens at the center. As the tree matures, it bears fruit known as elephant apples. These fruits are intriguing, with a rough, woody exterior that resembles a small, greenish-yellow apple. When cut open, the fruit reveals a juicy, tart pulp with a distinct tangy flavor. It is often used in traditional culinary preparations, jams, jellies, and refreshing beverages. Apart from its aesthetic and culinary significance, the elephant apple tree also holds medicinal properties. Various parts of the tree, including the leaves, fruits, and bark, are used in traditional medicine for their therapeutic benefits. They are believed to possess antimicrobial, anti-inflammatory, and antioxidant properties, contributing to their use in herbal remedies. The bark and leaves are used as a laxative and astringent and the bark is also used as a mouthwash to treat thrush.

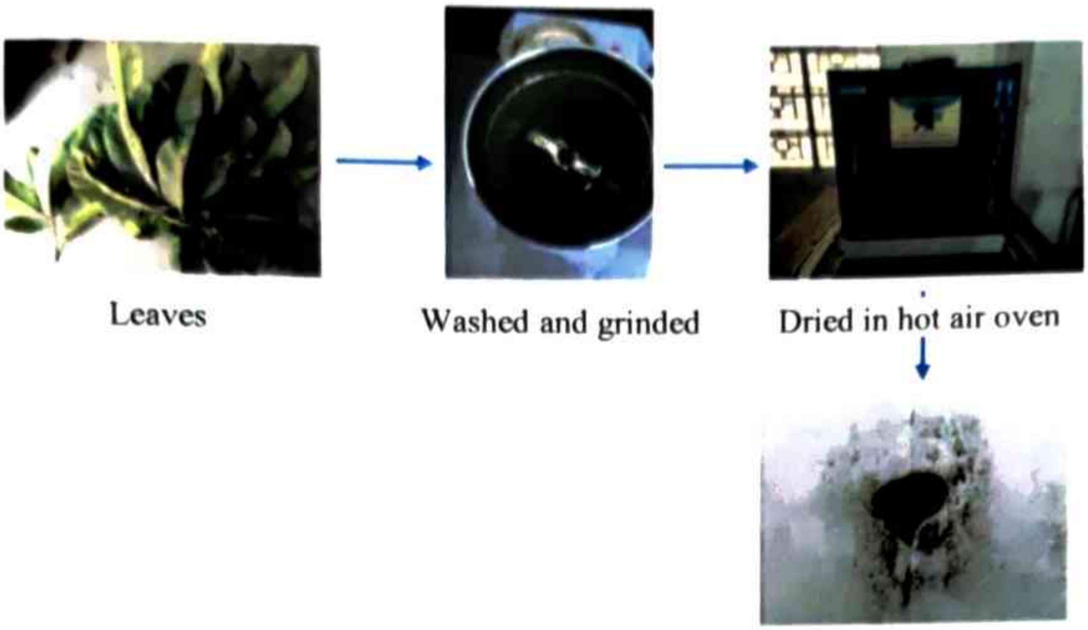
Fig 3.6: *Elephant Apple Tree*

3.9. ADSORBENTS PREPARED

All the adsorbents were prepared from the leaves, bark and fruit of Elephant Apple Tree or Ou Tenga tree. Apart from that, the commercially available activated charcoal was also used as the adsorbent in the experiments to compare against it the fluoride removal capacity of the prepared adsorbents.

3.9.1. ELEPHANT APPLE LEAF POWDER

The leaves which were used had been collected from locally growing Elephant Apple trees in the Lokhra area of Guwahati, Assam. They were cleaned thoroughly with distilled water to remove the dirt and impurities and were then sun dried for 2 days. The dried leaves were then crushed and grinded into fine powder which was then sieved to obtain less than 300 micrometer sized particles. After that it was dried in a hot air oven at a temperature of 100±5 °C for 2 hours to completely remove any moisture from it. This was the required powder which was to be tested for its fluoride removal capacity. The pictorial representation of the formation of ELP is shown in the Figure 3.7 below.



Leaves

Washed and grinded

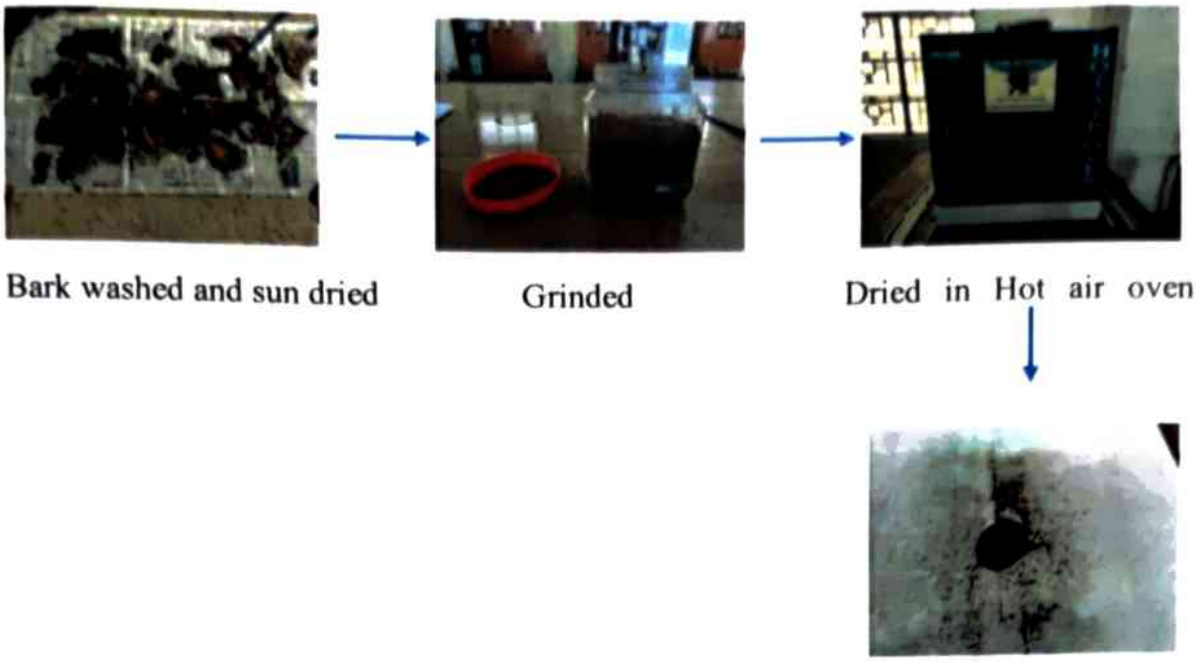
Dried in hot air oven

ELP for adsorption studies

Fig 3.7: ELP Preparation Process

3.9.2. ELEPHANT APPLE BARK POWDER

The bark of the Elephant Apple tree was collected and washed with distilled water thoroughly to remove the dirt and impurities from it and was then sun dried for 2 days. The dried bark was then cut into small pieces and grinded to a powder form which was sieved to obtain less than 300 micrometer sized particles. This was then dried in a hot air oven at a temperature of 100±5 °C for 2 hours to completely remove any moisture from it. This was the required powder which was to be tested for its fluoride removal capacity. The pictorial representation of the formation of EBP is shown in the Figure 3.8 below.



Bark washed and sun dried

Grinded

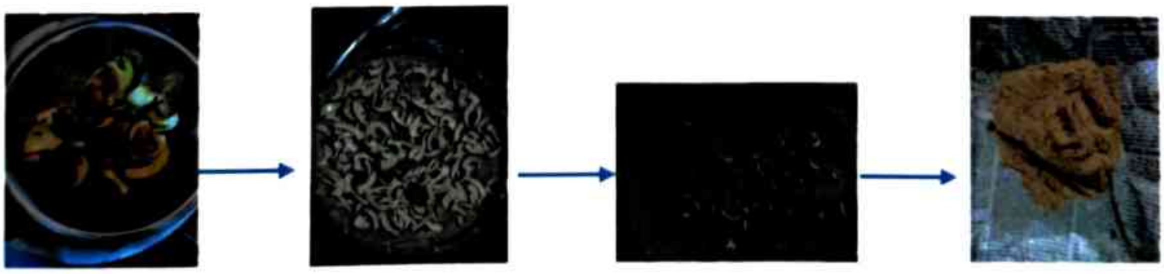
Dried in Hot air oven

EBP for adsorption studies

Fig 3.8: EBP Preparation Process

3.9.3. ELEPHANT APPLE FRUIT POWDER

The Elephant Apple fruit was locally purchased. The bulk of the fruit consist of thick sepals which were washed properly with distilled water and then cut into small pieces and were left to be sun dried for 3 to 4 days. The dried parts were then grinded into powder form and then sieved to obtain less than 300 micrometer sized particles. As the sun drying was enough to completely remove all the moisture from it, they were not dried in the oven and were tested for their fluoride removal capacity. The pictorial representation of the formation of EFP is shown in the Figure 3.9 below.



Fruit

Washed and cut

Sun dried

Grinded to obtain EFP

Fig 3.9: EFP Preparation Process

3.9.4. CARBONIZED ELEPHANT APPLE LEAF POWDER

The conditioned Elephant Apple leaf powder was carbonized in a muffle furnace at the carbonization temperature of 550 °C with a heating rate of 10 °C/min for a carbonization time of 2 hours. The carbonization step was carried out in Indian Institute of Technology, Guwahati. The char obtained was tested for its fluoride removal capacity. The pictorial representation of the formation of CELP is shown in the Figure 3.10 below.

Conditioned ELP Carbonization CELP for adsorption studies

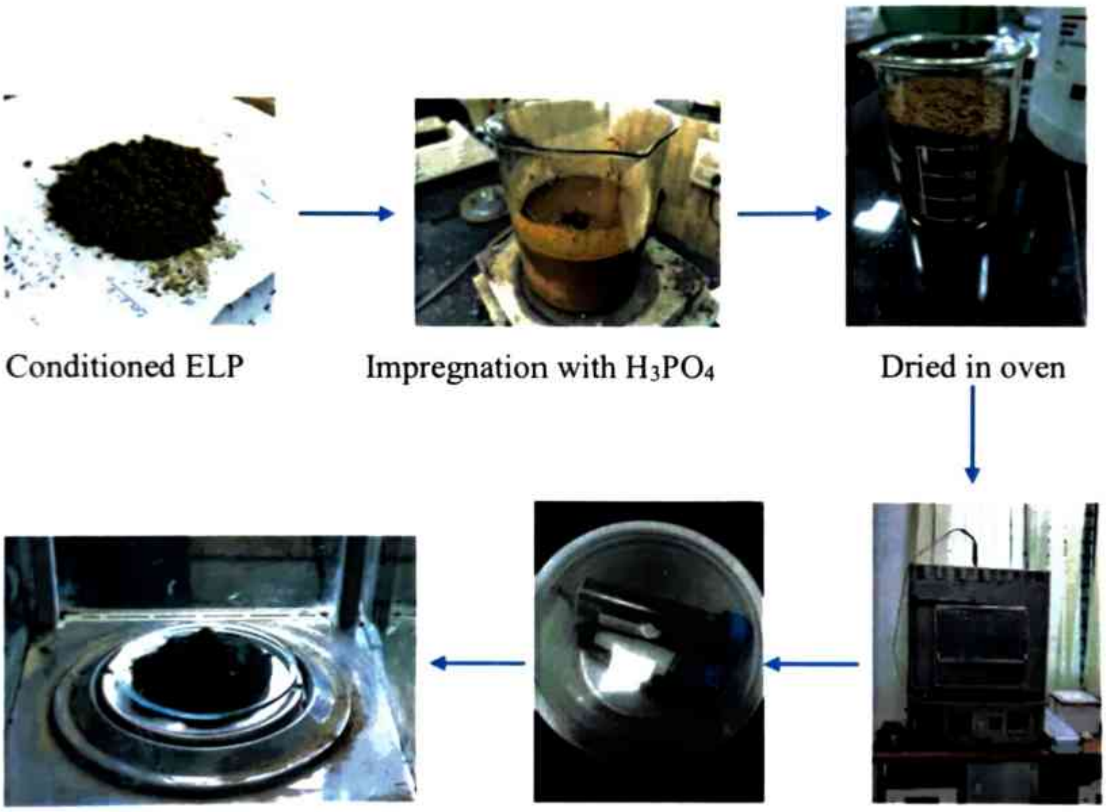
Fig 3.10: CELP Preparation Process

3.9.5. CARBONIZED ELEPHANT APPLE LEAF POWDER IMPREGNATED WITH H_3PO_4

Activated carbons can be generated either by physical or chemical activation. The chemical reagents generally employed in the chemical activation of lignocellulosic residues are $ZnCl_2$, H_3PO_4 etc. The chemical activation procedure based on wet impregnation with H_3PO_4 was chosen because of the potential environmental risk of using $ZnCl_2$.

The conditioned Elephant Apple leaf powder were impregnated with 20% w/w H_3PO_4 solution. The sample was then stirred at a constant rate of stirring for 2 hours in the magnetic stirrer and was then left to settle for a week. After that, the solution was removed by gravitational filtration and the solid was dried in an oven at a temperature of 100±5 °C for 24 hours. After the sample was completely dried, it was then subjected to carbonization in a muffle furnace with a heating rate of 10 °C/min and a carbonization time of 2 hours. Carbonization temperature of 550 °C was allowed at the end of which char was obtained.

This product was then subjected to washing with hot distilled wash water and 5% w/w NaOH solution to remove any remaining phosphoric acid and dirt and impurities that may have fallen or generated during the carbonization procedure. The washing was done for several doses till a pH of around 5 was obtained in the effluent wash water. After the completion of the washing procedure, the product was again dried in a hot air oven at a temperature of 100±5 °C for 24 hours at the end of which the required adsorbent sample was obtained which was to be tested for its fluoride removal capacity. The pictorial representation of the formation of CELP-H_3PO_4 is shown in the Figure 3.11 below.



Conditioned ELP

Impregnation with H_3PO_4

Dried in oven

CELP-H_3PO_4 for adsorption studies

Washing of char

Carbonization

Fig 3.11: *CELP-H_3PO_4 Preparation Process*

3.9.6. COMMERCIALLY AVAILABLE ACTIVATED CHARCOAL

Activated charcoal is considered to be the most available and important commercial adsorbents, with larger chemical surface area used in various significant areas. It is used in the environment for the purification of water in commercial sources as well as in industrial waste water management. It is a form of carbon consisting of low volume pores in a small size, so it has a big molecular surface area available for several chemical reactions and for adsorption. The low volume pores make the carbon possess a large surface area for effective adsorption and higher the surface area of the adsorbent the higher will be the absorbance.

The commercially available activated charcoal was used as the adsorbent that was bought earlier by the department to know its fluoride removal capacity as well as to compare the removal capacity of the adsorbents that were prepared against it.

Fig 3.12: *Commercially Available Activated Charcoal*

3.10. FLUORIDE ADSORPTION STUDIES

The defluoridation study was conducted by preparing a fluoride stock solution and batch adsorption experimentations were done. The fluoride stock solution was prepared by dissolving 0.0221 g NaF salt in 1000 ml distilled water to prepare 10 ppm fluoride solution. This stock solution was then diluted to the required concentrations using distilled water for the testing of the adsorbents.

For each of the adsorbent, the experiment was conducted by taking 500 ml of the fluoride solution of required concentration and mixing the adsorbent powder in it in the required dosage. The temperature was set at 25 °C and the rate of stirring was kept constant for the entirety of the experimentation using a magnetic stirrer. The fluoride removal capacity of the adsorbents was studied for different contact times by collecting the samples at set time intervals. The samples collected were then allowed a settlement time of 10 to 15 minutes after which they were filtered using Whatman filter papers till a clear solution was obtained. These samples were then stored in plastic containers and were then tested for their fluoride content.

The testing of the Elephant Apple leaf and fruit powders were done for the initial fluoride ion concentration of 5 ppm. The temperature was set at 25 °C and the rate of stirring was kept constant. An adsorbent dosage of 2 g/L was used and the samples were collected in predetermined time intervals from 10 to 50 minutes (10, 20, 30, 40 and 50 minutes).

The testing of the Elephant Apple bark powder was done for the initial fluoride ion concentration of 5 ppm. The temperature was set at 25 °C and the rate of stirring was kept constant. An adsorbent dosage of 2 g/L was used and the samples were collected in predetermined time intervals from 10 to 30 minutes (10, 20 and 30 minutes).

The testing of the carbonized Elephant Apple leaf powder was done for the initial fluoride ion concentration of 5 ppm. The temperature was set at 25 °C and the rate of stirring was kept constant. An adsorbent dosage of 2 g/L was used and the samples were collected in predetermined time intervals from 15 to 75 minutes (15, 30, 45, 60 and 75 minutes).

The testing of the carbonized Elephant Apple leaf powder impregnated with H_3PO_4 was carried out for three different initial fluoride ion concentrations of 3 ppm, 5 ppm and 7 ppm. The temperature was set at 25 °C and the rate of stirring was kept constant. An adsorbent dosage of 2 g/L was used and the samples were collected in predetermined time intervals from 30 to 120 minutes (30, 60, 80, 100, 120 minutes).

The testing of the commercially available activated charcoal was done for the initial fluoride ion concentration of 5 ppm. The temperature was set at 25 °C and the rate of stirring was kept constant. An adsorbent dosage of 2 g/L was used and the samples were collected in predetermined time intervals. It was tested two times; the first time between the time intervals of 10 to 50 minutes (10, 20, 30, 40, 50 minutes) and the second time between the time intervals of 15 to 75 minutes (15, 30, 45, 60 and 75 minutes).

The analysis of the water samples was done using Orion Star™ A214 pH/ISE Meter and it was carried out at Pollution Control Board, Assam. For the analysis, the fluoride selective electrode was first calibrated by two-point calibration for concentration range of 1 ppm to 10 ppm using an analytical grade fluoride stock solution. After the calibration, the fluoride ion concentration of the samples was measured after adding TISAB to the samples in the ratio of 1:1 (5 ml each) for decomplexation of the fluoride ions. The electrode was then inserted in the sample and the readings were noted.

CHAPTER 4

OBSERVATIONS AND RESULTS

4.1. ELEPHANT APPLE LEAF POWDER

The defluoridation potential of the adsorbent Elephant Apple Leaf Powder (ELP) was determined for dosage of 2 g/L by varying the contact time between 10 to 50 minutes with the initial fluoride concentration of 5 ppm at 25 °C and a constant rate of stirring. The results obtained have been tabulated below.

Initial fluoride ion concentration = 4.22 ppm				
Sl. No.	**Contact time (minutes)**	**Fluoride Concentration (ppm)**	**Fluoride removed (ppm)**	**Removal percentage**
1	10	4.13	0.09	2.13%
2	20	4.06	0.16	3.79%
3	30	3.96	0.26	6.16%
4	40	4.11	0.11	2.61%
5	50	4.21	0.01	0.23%

Table 4.1: *Fluoride removal percentage of ELP*

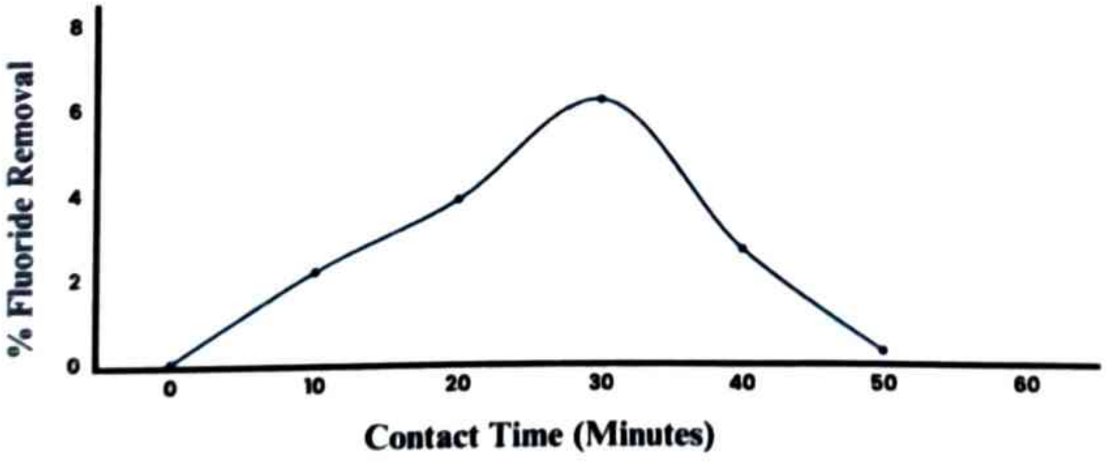


Fig 4.1: *Contact time vs % Fluoride removal of ELP*

The Figure 4.1 shows that the fluoride removal percentage is less than 10% for the different contact times with maximum amount of 6.16% being removed at the contact time of 30 minutes. After 30 minutes, the removal percentage decreased indicating that the fluoride uptake by the adsorbent decreased and the maximum amount of adsorption of fluoride ions for the given setup occurred at the contact time of 30 minutes and further contact would not increase the fluoride removal from the water sample.

4.2. ELEPHANT APPLE BARK POWDER

The defluoridation potential of the adsorbent Elephant Apple Bark Powder (EBP) was determined for dosage of 2 g/L by varying the contact time between 10 to 30 minutes with the initial fluoride concentration of 5 ppm at 25 °C and a constant rate of stirring. The results obtained have been tabulated below.

Initial fluoride ion concentration = 4.22 ppm				
Sl. No.	**Contact time (minutes)**	**Fluoride Concentration (ppm)**	**Fluoride removed (ppm)**	**Removal percentage**
1	10	4.05	0.17	4.03%
2	20	4.04	0.18	4.26%
3	30	4.17	0.05	1.18%

***Table 4.2:** Fluoride removal percentage of EBP*

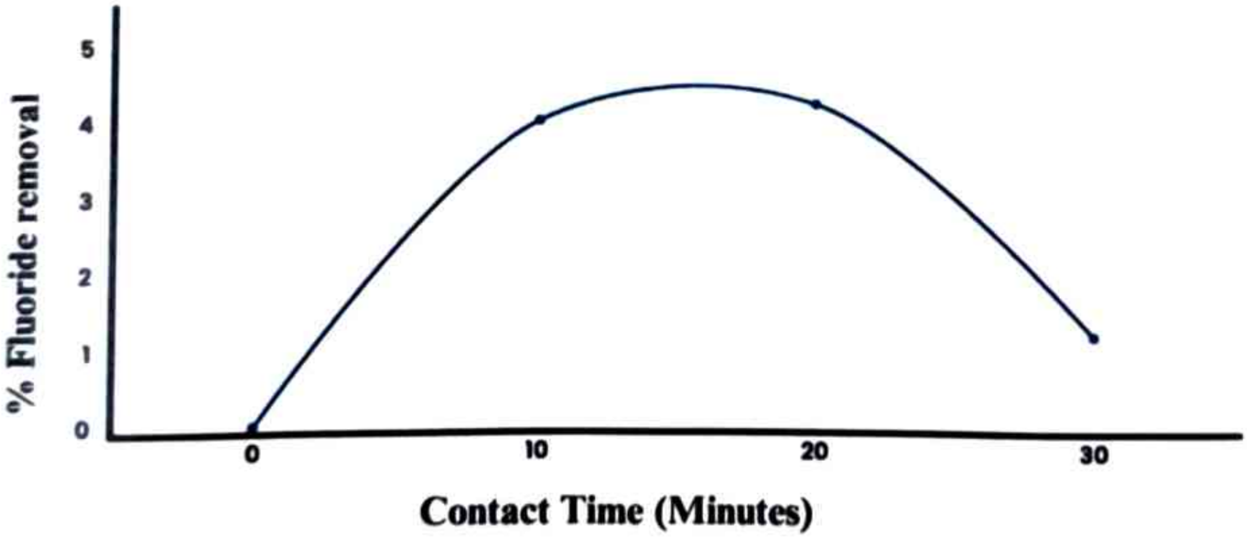


***Fig 4.2:** Contact time vs % Fluoride removal of EBP*

The Figure 4.2 shows that the fluoride removal percentage is less than 10% for the different contact times with the maximum amount of 4.26 % being removed at the contact time of 20 minutes. The fluoride uptake by the EBP is very less and a satisfactory removal of fluoride ions from the water samples was not found.

4.3. ELEPHANT APPLE FRUIT POWDER

The defluoridation potential of the adsorbent Elephant Apple Fruit Powder (EFP) was determined for dosage of 2 g/L by varying the contact time between 10 to 50 minutes with the initial fluoride concentration of 5 ppm at 25 °C and a constant rate of stirring. The results obtained have been tabulated below.

Initial fluoride ion concentration = 4.16 ppm				
Sl. No.	**Contact time (minutes)**	**Fluoride Concentration (ppm)**	**Fluoride removed (ppm)**	**Removal percentage**
1	10	4.02	0.14	3.36%
2	20	3.95	0.21	5.05%
3	30	4.06	0.1	2.4%
4	40	4.06	0.1	2.4%
5	50	4.12	0.04	0.96%

***Table 4.3:** Fluoride removal percentage of EFP*

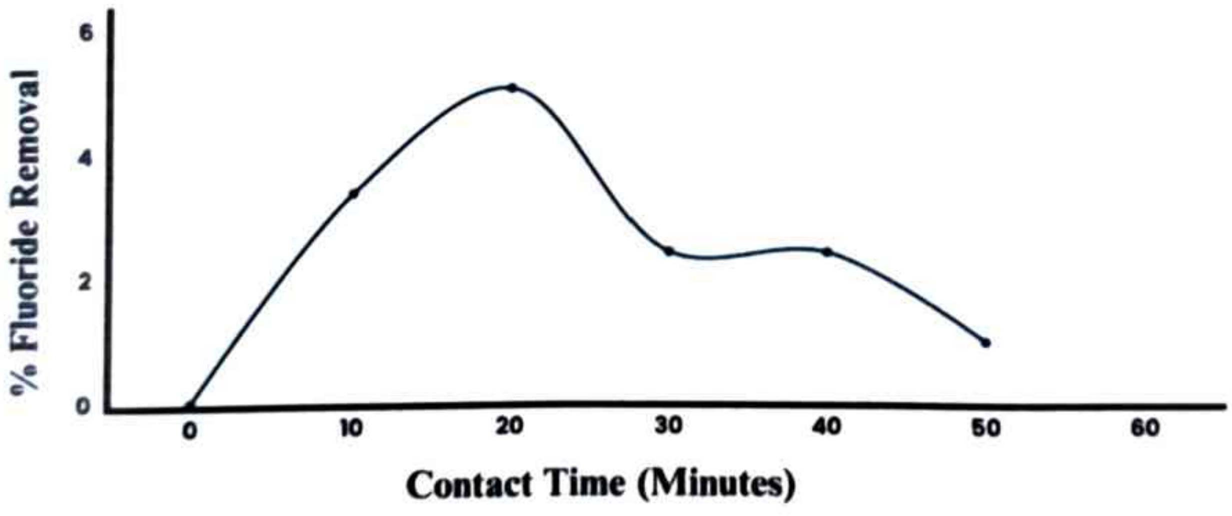


***Fig 4.3:** Contact time vs % Fluoride removal of EFP*

The Figure 4.3 shows that the fluoride removal percentage is less than 10% for the different contact times with the maximum amount of 5.05% being removed at the contact time of 20 minutes. After 20 minutes, the removal percentage decreased indicating that the fluoride uptake by the adsorbent decreased and the maximum amount of adsorption of fluoride ions for the given setup occurred at the contact time of 20 minutes and further contact would not increase the fluoride removal from the water sample.

4.4. CARBONIZED ELEPHANT APPLE LEAF POWDER

The preparation of Carbonized Elephant Apple Leaf Powder (CELP) was done by taking 10 g of the conditioned ELP and the final amount of CELP obtained was 2.09 g thereby giving a production yield of 20.9%. The pH in the effluent wash water was 10.08. The defluoridation potential of the adsorbent CELP was determined for dosage of 2 g/L by varying the contact time between 15 to 75 minutes with the initial fluoride concentration of 5 ppm at 25 °C and a constant rate of stirring. The results obtained have been tabulated below.

Initial fluoride ion concentration = 4.25 ppm				
Sl. No.	**Contact time (minutes)**	**Fluoride Concentration (ppm)**	**Fluoride removed (ppm)**	**Removal percentage**
1	15	4.04	0.21	4.94%
2	30	4.07	0.18	4.23%
3	45	3.99	0.26	6.12%
4	60	4.05	0.2	4.71%
5	75	4.09	0.16	3.76%

Table 4.4: *Fluoride removal percentage of CELP*

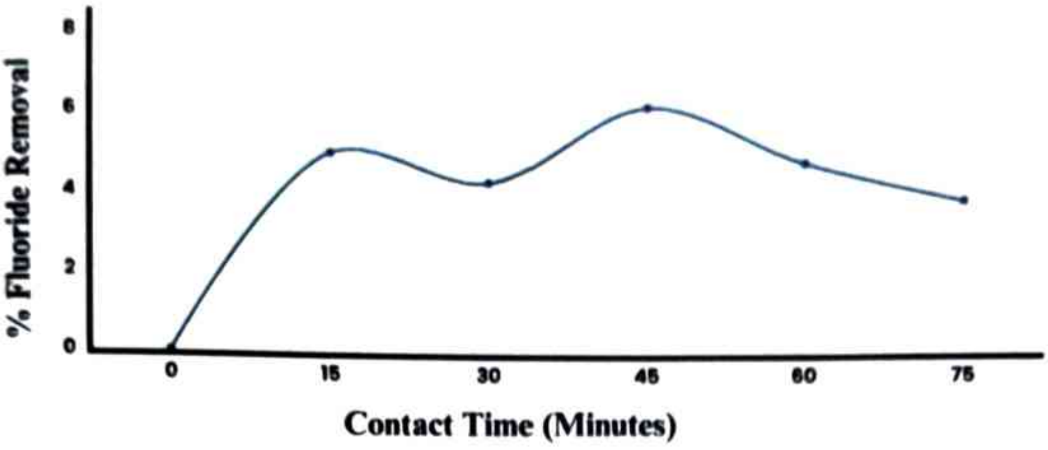


Fig 4.4: *Contact time vs % Fluoride removal of CELP*

The Figure 4.4 shows that the fluoride removal percentage is less than 10% for the different contact times with the maximum amount of 6.12% being removed at the contact time of 45 minutes. The fluoride uptake by the adsorbent kept increasing and reached the maximum at 45 minutes and then it decreased indicating that optimal contact time for the given setup would be 45 minutes and further contact would not increase the fluoride removal from the water sample. The fluoride removal capacity of CELP is seen to be slightly better than EBP and EFP and almost similar to ELP with the maximum removal being observed at 30 minutes for ELP and 45 minutes in the case of CELP.

4.5. CARBONIZED ELEPHANT APPLE LEAF POWDER IMPREGNATED WITH H_3PO_4

The preparation of Carbonized Elephant Apple Leaf Powder Impregnated with H_3PO_4 (CELP-H_3PO_4) was done by taking 50 g of the conditioned ELP and the final amount of CELP-H_3PO_4 obtained was 10.72 g thereby giving a production yield of 21.44%. The pH in the effluent wash water was 4.30. The defluoridation experiment for CELP-H_3PO_4 was first done for the initial fluoride concentration of 5 ppm with the adsorbent dosage of 2 g/L at 25 °C, a constant rate of stirring and by varying the contact time between 10 to 60 minutes. The results obtained have been tabulated below.

Initial fluoride ion concentration = 4.12 ppm				
Sl. No.	**Contact time (minutes)**	**Fluoride Concentration (ppm)**	**Fluoride removed (ppm)**	**Removal percentage**
1	10	3.16	0.96	23.3%
2	20	3.21	0.91	22.09%
3	30	3.14	0.98	23.78%
4	40	3.18	0.94	22.81%
5	50	3.13	0.99	24.03%
6	60	2.91	1.21	29.37%

***Table 4.5:** Fluoride removal percentage of CELP-H_3PO_4*

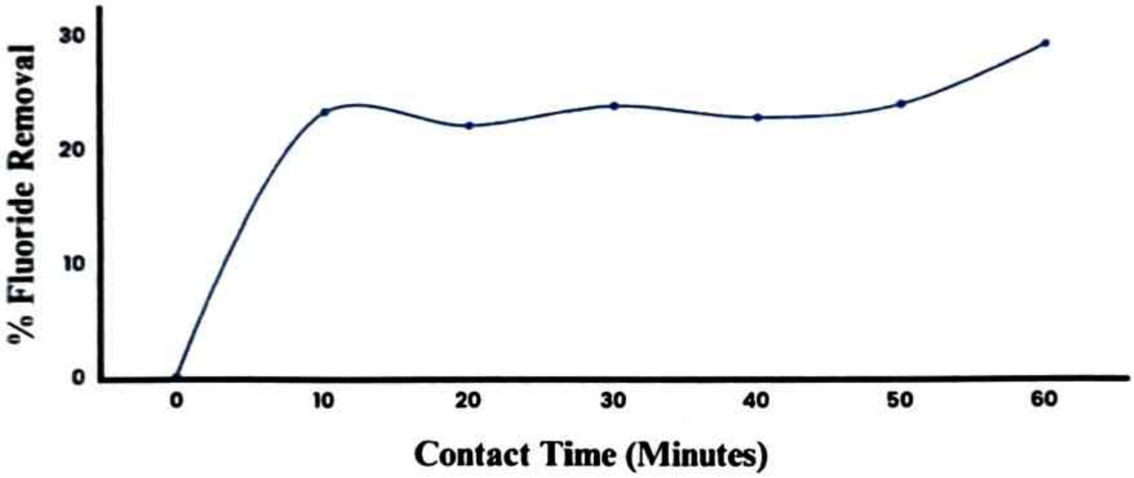


***Fig 4.5:** Contact time vs % Fluoride removal of CELP-H_3PO_4*

The Figure 4.5 shows that a maximum fluoride removal of 29.37% had been obtained for the contact time of 60 minutes. It can be seen that the maximum uptake of fluoride ions had not been achieved and by increasing the contact time, further removal would be possible.

Therefore, the experiment was conducted again by increasing the contact time and varying it between 30 to 120 minutes. The rest of the parameters were kept constant and the results obtained have been tabulated below.

Initial fluoride ion concentration = 4.25 ppm				
Sl. No.	**Contact time (minutes)**	**Fluoride Concentration (ppm)**	**Fluoride removed (ppm)**	**Removal percentage**
1	30	3.06	1.19	28%
2	60	2.86	1.39	32.71%
3	80	2.86	1.39	32.71%
4	100	2.96	1.29	30.35%
5	120	3.00	1.25	29.41%

Table 4.6: *Fluoride removal percentage of CELP-H_3PO_4 having initial fluoride concentration of 5 ppm*

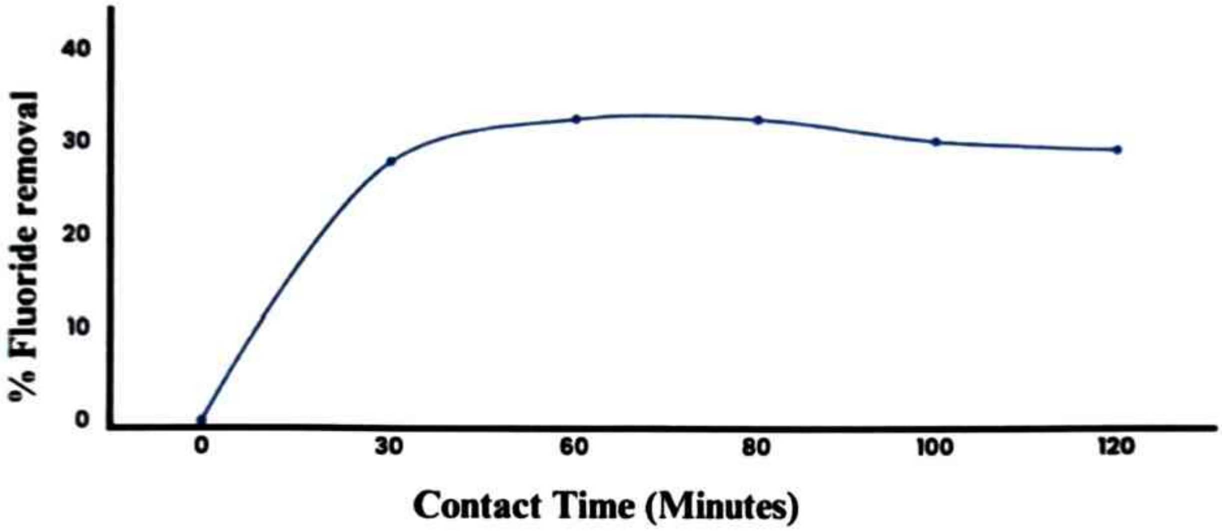


Fig 4.6: *Contact time vs % Fluoride removal of CELP-H_3PO_4 having initial fluoride concentration of 5 ppm*

The Figure 4.6 shows that the maximum fluoride removal of 32.71% had been obtained between 60 and 80 minutes. The fluoride uptake by the adsorbent started to decrease after 80 minutes thereby indicating that the peak adsorption by CELP-H_3PO_4 takes place between the contact time of 60 to 80 minutes for the given setup. The fluoride removal capacity of CELP-H_3PO_4 is seen to be very high as compared to the rest of the adsorbents.

The initial fluoride concentration was then varied and the test was conducted by first taking the initial fluoride concentration as 3 ppm and then as 7 ppm. The adsorbent dosage was taken as 2 g/L at 25 °C, a constant rate of stirring and the contact time was varied between 30 and 120 minutes. The results obtained are tabulated below and a comparison among the fluoride removal capacity of the CELP-H_3PO_4 for the varying initial fluoride concentration have been done.

Initial fluoride ion concentration = 2.47 ppm				
Sl. No.	**Contact time (minutes)**	**Fluoride Concentration (ppm)**	**Fluoride removed (ppm)**	**Removal percentage**
1	30	1.54	0.93	37.65%
2	60	1.58	0.89	36.03%
3	80	1.22	1.25	50.61%
4	100	1.45	1.02	41.29%
5	120	1.49	0.98	39.68%

Table 4.7: *Fluoride removal percentage of CELP-H_3PO_4 having initial fluoride concentration of 3 ppm*

Initial fluoride ion concentration = 6.06 ppm				
Sl. No.	**Contact time (minutes)**	**Fluoride Concentration (ppm)**	**Fluoride removed (ppm)**	**Removal percentage**
1	30	4.47	1.59	26.24%
2	60	4.66	1.4	23.10%
3	80	4.44	1.62	26.73%
4	100	4.24	1.82	30.03%
5	120	4.44	1.62	26.73%

Table 4.8: *Fluoride removal percentage of CELP-H_3PO_4 having initial fluoride concentration of 7 ppm*

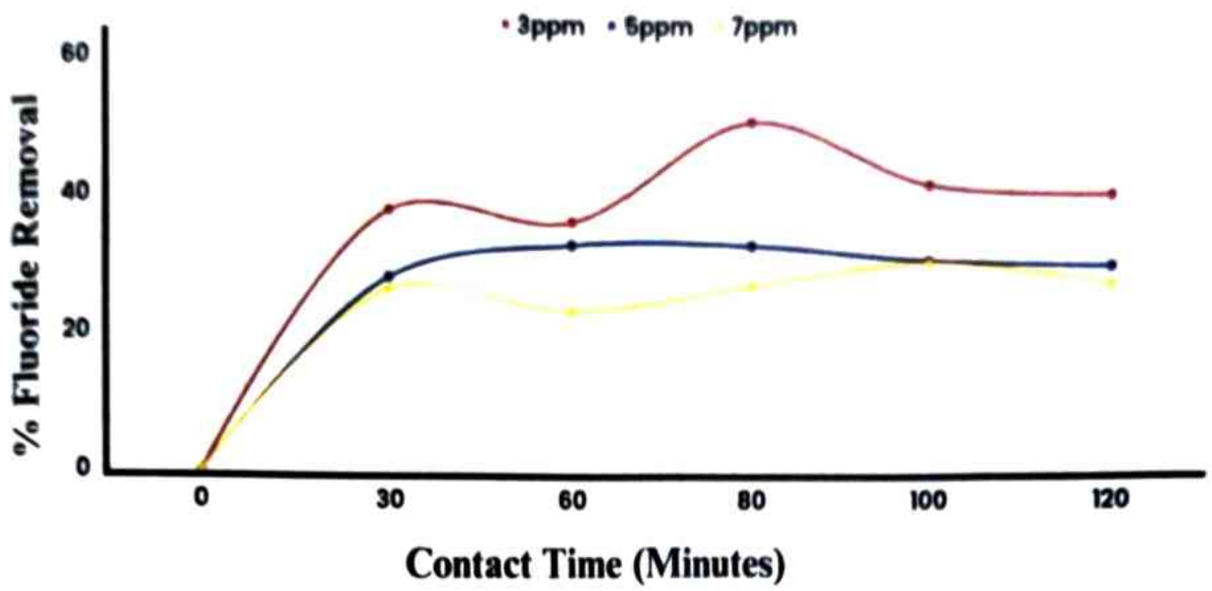


Fig 4.7: Contact time vs % Fluoride removal of CELP-H_3PO_4 having initial fluoride concentrations of 3 ppm, 5 ppm and 7 ppm

The figure 4.7 shows that the maximum removal of fluoride had been obtained by the adsorbent CELP-H_3PO_4 with the initial fluoride concentration of 3 ppm. For 3 ppm initial fluoride concentration, maximum removal of 50.61% had been observed and similarly, for 5 ppm initial fluoride concentration, maximum removal of 32.71% had been obtained and for 7 ppm initial fluoride concentration, maximum removal of 30.03% had been obtained. It is seen that the maximum removal for both 3 ppm and 5 ppm solution had been obtained at the contact time of 80 minutes and for the 7 ppm solution, it is at 100 minutes. The fluoride removal capacity of CELP-H_3PO_4 increases as the initial fluoride concentration decreases.

4.6. COMMERCIALLY AVAILABLE ACTIVATED CHARCOAL

The defluoridation experiment of the Commercially Available Activated Charcoal (CAC) was conducted two times by changing the contact time intervals. The first study was conducted for the time intervals 10 to 50 minutes and the second study was conducted by varying the time intervals between 15 to 75 minutes. The initial fluoride concentration was taken as 5 ppm, adsorbent dosage was taken as 2 g/L at 25 °C and the rate of stirring was kept constant for both the experiments. The results obtained have been tabulated below.

Initial fluoride ion concentration = 4.27 ppm				
Sl. No.	**Contact time (minutes)**	**Fluoride Concentration (ppm)**	**Fluoride removed (ppm)**	**Removal percentage**
1	10	3.95	0.32	7.49%
2	20	3.99	0.28	6.56%
3	30	4	0.27	6.32%
4	40	3.96	0.31	7.26%
5	50	4	0.27	6.32%

Table 4.9: *Fluoride removal percentage of CAC between the time intervals 10 to 50 minutes*

Initial fluoride ion concentration = 4.21 ppm				
Sl. No.	**Contact time (minutes)**	**Fluoride Concentration (ppm)**	**Fluoride removed (ppm)**	**Removal percentage**
1	15	3.98	0.23	5.46%
2	30	4.09	0.12	2.85%
3	45	4.11	0.10	2.38%
4	60	4.04	0.17	4.04%
5	75	4.07	0.14	3.32%

Table 4.10: *Fluoride removal percentage of CAC between the time intervals 15 to 75 minutes*

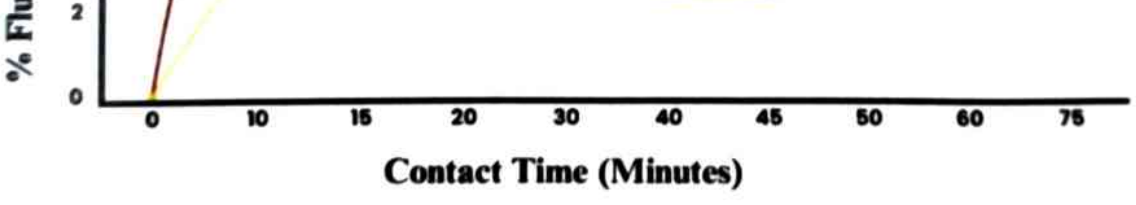


Fig 4.8: *Contact time vs % Fluoride removal of CAC-I having time intervals between 10 to 50 minutes and CAC-II having time intervals between 15 to 75 minutes*

The Figure 4.8 shows that the fluoride removal for CAC in both the cases followed the same trend and almost similar fluoride removal had been obtained. The commercial activated charcoal should have had a maximum fluoride removal of around 94% at the optimum conditions as per the study conducted by Tembhurkar et al. (2006) but it had not been the case during the experimentation. The experiment had been done two times and almost similar results had been obtained in both the cases. This shows that there had been no error while doing the experiment. The low adsorption of fluoride ions by the CAC could have been the result of the adsorbent itself being contaminated.

The maximum fluoride removal by CAC had been observed to be 7.49%. On comparing it with the rest of the adsorbents, it is seen that the maximum fluoride removal capacity of ELP (6.16%), EBP (4.26%), EFP (5.05%) and CELP (6.12%) are less than that of CAC. However, the maximum fluoride removal capacity of CELP-H_3PO_4 is much higher than that of CAC with the former having 50.61% fluoride removal at the optimum condition. The optimum conditions as observed for CELP-H_3PO_4 are an initial fluoride concentration of 3 ppm, adsorbent dosage of 2 g/L, operating temperature of 25 °C, a constant rate of stirring with the contact time of 80 minutes.

Thus, it is seen that CELP-H_3PO_4 is an efficient adsorbent and it can be used effectively in removing fluoride ions from the ground water.

CHAPTER 5

CONCLUSION

Different materials and methods have been used for the preparation of adsorbents and the testing of the prepared adsorbents for their fluoride removal capacity have been done in this project work. Adsorbent using a bio based raw material was selected because of its easy availability and low cost and so all the adsorbents that were prepared were from the leaves, bark and fruit of the Elephant Apple tree. Five adsorbents have been prepared in this project work which are Elephant Apple Leaf Powder (ELP), Elephant Apple Bark Powder (EBP), Elephant Apple Fruit Powder (EFP), Carbonized Elephant Apple Leaf Powder (CELP) and Carbonized Elephant Apple Leaf Powder impregnated with H_3PO_4 (CELP-H_3PO_4). The performance of these adsorbents have been tested for different contact times and they have been compared against each other as well as against the commercially available activated charcoal (CAC). Batch adsorption studies were carried out and for the initial fluoride concentration of 5 ppm, adsorbent dosage of 2 g/L, operating temperature of 25 °C, a constant rate of stirring and optimal contact time, the maximum fluoride removal for ELP was 6.16%, for EBP it was 4.26%, for EFP it was 5.05%, for CELP it was 6.12%, for CELP-H_3PO_4 it was 32.71% and for CAC it was 7.49%. The initial fluoride content for the testing of CELP-H_3PO_4 was varied and for the initial fluoride concentration of 3 ppm, the maximum fluoride removal of 50.61% was obtained for the optimal conditions. Thus, the above results fulfil all the objectives drawn for the study.

CELP-H_3PO_4 is a capable adsorbent and further studies on it by varying the other parameters can be done. The other parameters like adsorbent dosage, pH of the solution, rate of agitation, initial fluoride concentration, operating temperatures etc can be varied and studies can be conducted. The surface morphology, structure, adsorption isotherms, adsorption kinetics need to be studied in detail. More detailed studies on the adsorbent can also lead to achieving higher fluoride removal efficiencies and in finding the optimal conditions for it to work effectively. Along with it, the adsorbent can also be studied to see if it is capable of removing other harmful components present in the ground water.

It is concluded from all the experiments and observations that CELP-H_3PO_4 is an effective and efficient as well as economical adsorbent for the removal of fluoride ions from ground water. This capable adsorbent should be studied in detail and it should be optimised so that its full potential can be estimated.

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Water Quality Analysis in and around Deepor Beel

Submitted in partial fulfillment of the requirement for
The Degree of Bachelor of Technology
in
Chemical Engineering
of
Assam Science and Technology University

Session: 2019-2023

Submitted By-

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Certificate

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Dr. Bandana Chakrabarty
Head of Department
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DECLARATION

We declare that this written submission represents our ideas in our own words and where others' ideas or words have been included, we have adequately cited and referenced the original sources. We also declare that we have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in our submission. We understand that any violation of the above will be cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

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PROJECT AT A GLANCE

The present paper focuses on the study of water quality analysis parameters such as pH, conductivity, dissolved oxygen, biological oxygen demand, chemical oxygen demand, chloride test, total dissolved solids, total suspended solids of the Deepor Beel. The standard water quality analysis tests were conducted to know about the levels of contamination in the entire stretch of the Deepor Beel to suggest appropriate solutions. Results of the assessment of various parameters established that encroachment and dumping of the household and commercial waste into the periphery of the river have caused severe degradation of the Lake. The city is drained mainly by Deepor bill which is the only Ramsar site of North East. Both domestic and industrial effluents affect the water quality through direct toxic action or quantitative alteration in the character of the river. Deepor bill acting as a natural drain for the people of Guwahati, has been reduced to a stagnant water body with very high toxicity levels. With the increment of pollution levels all throughout, the suitability of a water body for drinking, commercial and industrial purposes is a very common concern. Consequently, strategic and planned moves must be implemented and brought into action for the full-fledged recovery of the lake Deepor Beel. Public awareness and participation should be brought into effect along with constant monitoring to revamp its poor condition.

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CHAPTER 1

INTRODUCTION

Population of the world is growing rapidly and urban population in the urban centres has been a pressure for the existing infrastructure like water supply, drainage, sanitation facilities. Rural push and urban pull are the result of migration towards the cities. Huge migration in search of job, education and better lifestyle is the cause of conversion of peri urban areas into urban sub centres. Urbanization is the root cause of environmental degradation and natural resources depletion.

Guwahati being the gateway to North Eastern India and an important centre for economic, social, educational, commercial and transportation activities. The city has experienced urban growth and urbanization which results in various environmental problems.

Deepor Beel is a permanent freshwater lake and the only Ramsar site in Assam is Experiencing adverse human activities; filling of wetlands for habitation purpose, cutting the sides of wetlands, pollution, fishing, killing of migratory birds, excessive fodder practices etc. Degradation of water quality, sedimentation in the lake surface, deforestation activities in and around the Beel area has increased the importance of conservation and restoration of the Beel.

The study was initiated by understanding the importance of the ecosystem and effect of urbanization over the environment. Our final year project is intended to develop understanding of the cause of environmental degradation and to know the proposals and policies developed by the GMDA authority for the conservation and management of the Deepor Beel. The study is based on various secondary sources from books, internet, ENVIS booklets and discussion with our faculties.

1.1 OBJECTIVE

The aim and objectives are as follows:

- To study the quality of Deepor Beel by sampling from different location simultaneously
- To study the nature of pollution
- To quantify certain water quality parameters in the surface water.
- To study the variation in the contamination level from the station to station

CHAPTER 2

LITERATURE REVIEW

Various technical papers on Assessment of water quality for lakes have been presented at research level from which I referred many papers for study. These papers are presented below.

1. S. Chandra, A. Singh and P. K. Tomar [01] have described, lake water is a source of drinking and domestic use water for rural and urban population of India. The main goal of the present study was to assess drinking water quality of various lakes i.e. Porur lake Chennai, Hussain Sager Hyderabad Vihar lake Mumbai in India. For this, lakes water samples were collected from six different sites and composite sample prepared were analyzed for pH, turbidity, electrical conductivity (EC), total dissolved solids (TDS), total alkalinity (TA), total hardness (TH)and calcium hardness (Ca-H), chemical oxygen demand(COD), biochemical oxygen demand (BOD), dissolved oxygen (D.O.), sulphate (as SO_4^{2-}), nitrate (as NO_3) and chloride (Cl^-) levels .Some heavy metals like Iron, Zinc, Cadmium, Mercury, Nickel and Chromium were also analyzed in these samples. There were variations for EC (141-1041), turbidity (2-9 NTU), TDS (107.1–935.8 mg/L), SO_4^{2-} (4–8 mg/L), TA (42–410 mg/L), TH (41-280 mg/L), Ca–H (14- 10 mg/L), BOD (5-9mg/L), COD (4–32 mg/L) NO_3(1.1-3.6 mg/L) and Cl^- (49-167 mg/L) levels at different sites. Water pollution indicates that these parameters were manifold higher than the prescribed limit by the WHO & BIS standard.

2. V. Pradhan, M. Mohsin, B. H. Gaikwad [02] have studied, water quality of Chilika Lake was determined during the month of January 2012. It was observed that all the parameters are above the permissible limit except at the sample site S2. The results are discussed in the light of findings of other workers.

3. S. Hussaina, V. Maneb, et al. [03] have studied, In the present work we are reported the Physico chemical properties like pH, conductivity, Turbidity, TDS, DO, fluoride, chloride, Sodium, Sulphate, etc. and the values are compared for treated and untreated water samples. The samples were collected from a treatment plant in Ahmedpur, Dist Latur. The values change apparently after the treatment of water.

4. **R. M. Khan, M. J. Jadhav, I. R. Ustad [04]** have explained, in order to understand the water quality of Triveni Lake, Physio-chemical parameters were studied and analyzed for the period of one year i.e., December 2010 to November 2011. Various physicochemical parameters, such as water temperature, air temperature, pH, humidity, conductivity, free CO2, total solid, dissolved oxygen, Total alkalinity, Total hardness, $CaCO_3$, Ca^{2+}, Mg^{2+} were studied. The results revealed that there was significant seasonal variation in some physicochemical parameters and most of the parameters were in normal range and indicated better quality of lake water. It has been found that the water is best for drinking purposes in winter and summer seasons.

CHAPTER 3

SAMPLE COLLECTION

3.1 LOCATION FOR SAMPLE COLLECTION:

The Deepor Beel was once considered part of the Brahmaputra River in its southern embankment area, covering 40 km^2. It helps regulate the flood waters emerging from the city and Brahmaputra River during the south-west monsoon, and is thus a key stormwater storage facility for the city of Guwahati. It has been recognized as being of international importance since 2002 when it was categorized under the Ramsar Convention (No. 1207), to safeguard global biodiversity, and sustain human life through ecological and hydrological functions. The Beel is bounded by dense human populations in the north-east, and Rani and Garbhanga forest reserves in the south-east. Several suburbs and industrial complexes have been developed recently in parts of the wetland.

There are basically four points of collection of water sample-

- Site 1 (near Deepor Beel Wildlife Sanctuary)
- Site 2 (where most industries are located)
- Site 3 (near Dumping Site)
- Site 4 (near Hostel - 3 area)
- Site 5 (ASTU area)

Procedure of water sample collection

- Collection of water is done with a sterilized bucket from three different portions viz left bank, right bank, middle portion
- Water samples are collected in standard sterilized bottle and marked (i e sampling is done)
- Samples are brought to the laboratory and tested within 24 hours of duration, to avoid the change in properties of the water upon the action of bacterial cells onto it.

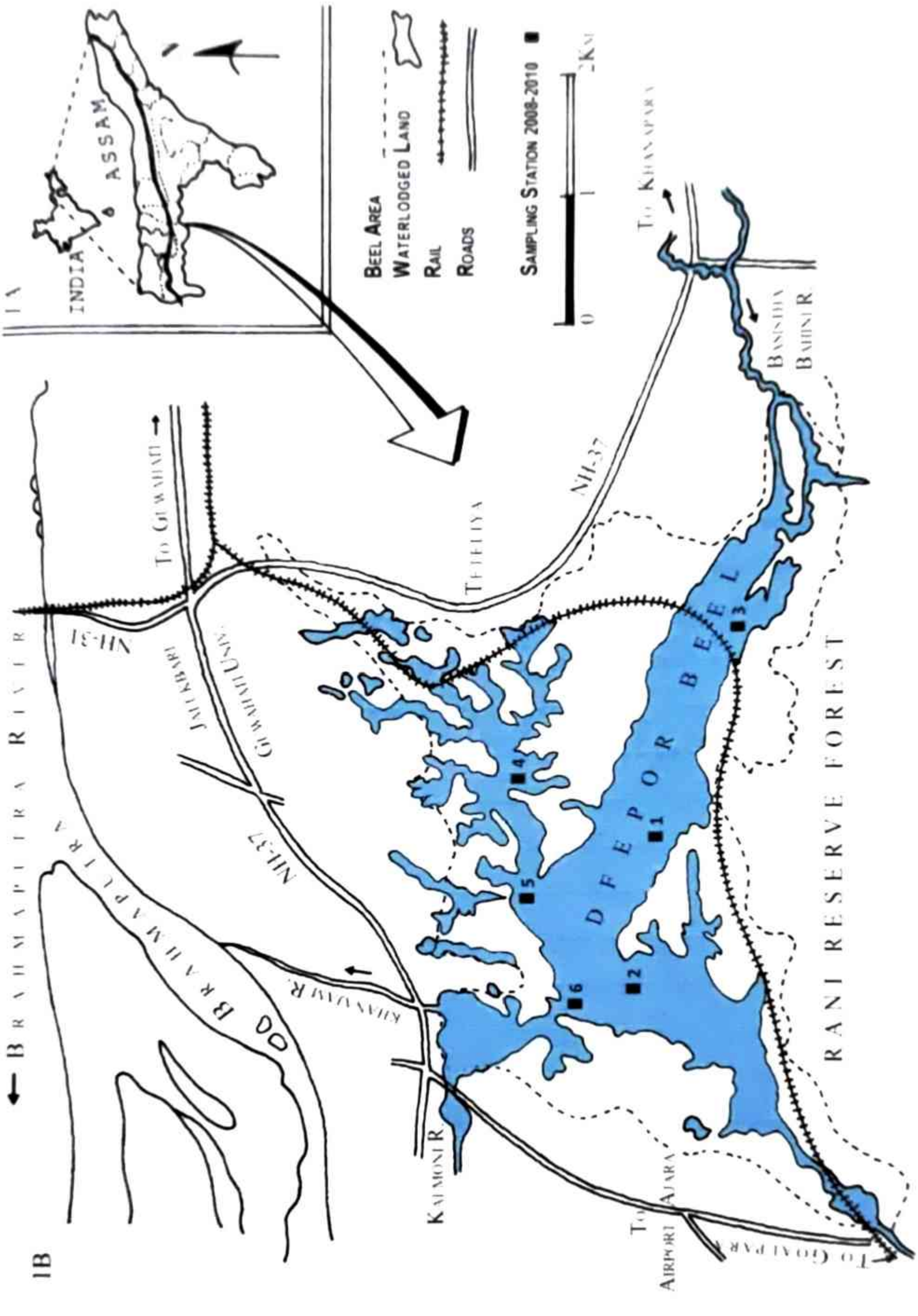

Fig 1: Deepor Beel Map

CHAPTER 4

MEASUREMENT OF VARIOUS PARAMETERS

There are many parameters which have been used for testing of the samples by different methods: -

1. pH
2. CONDUCTIVITY
3. DISSOLVED OXYGEN
4. TOTAL DISSOLVED SOLIDS
5. BIOLOGICAL OXYGEN DEMAND
6. CHEMICAL OXYGEN DEMAND
7. CHLORIDE
8. HARDNESS
9. TOTAL SUSPENDED SOLIDS

4.1 pH: pH, historically denoting "potential of hydrogen", is a scale used to specify the acidity or basicity of an aqueous solution. Acidic solutions are measured to have lower pH values than basic or alkaline solutions. The standard pH value of freshwater is 6.5 - 8.5.

Location	**pH**
Site 1	9
Site 2	9.2
Site 3	8.71
Site 4	7.5
Site 5	7.68

Table 4.1

4.2 Conductivity (Cell constant verification): Conductivity is a measure of the ability of water to pass an electrical current. Because dissolved salts and other inorganic chemicals conduct electrical current, conductivity increases as salinity increases. The standard conductivity value: 200 to 1000 mS/cm

Procedure:

1. Set the function and adjust the display to 1.000 with CAL control.
2. Dipping conductivity cell in a solution of known conduction. Here we took 1N KI solution.
3. Adjusting temperature to temperature of solution
4. Move the Function switch to cond. Position and range switch to appropriate range.
5. Adjust the cell constant knob so that the display reads the known value of the solution.
6. Bring the function switch to Cell Constant position.
7. The display shows the cell constant of the conductivity cell.

Location	Conductivity
• Site 1	262
• Site 2	458
• Site 3	395
• Site 4	284.25
• Site 5	312.5

Table 4.2

4.3 DO: Dissolved oxygen refers to the level of free, non – compound oxygen present in water or other liquids. It is an important parameter in assessing water quality because of its influence on the organisms living within a body of water.

Dissolved oxygen (DO) has been a fundamental requirement for plant and animal life in water. Reduction of DO is indicative of presence of substances collectively called oxygen demanding wastes. Decreased in the amount of DO indicates presence of large amounts of biodegradable organic matter which makes the water unacceptable as anaerobic decomposition of organic matter leads to septic conditions and production of noxious gases. The reagent used: 2ml manganese sulphate, 2ml alkali-iodide-azide, 2ml concentrated sulphuric acid, 2 ml starch solution and sodium thiosulfate. The following steps are taken to carry out the experiment to calculate the DO present in the sample:

1. We carefully fill a 300-mL glass Biological Oxygen Demand (BOD) stoppered bottle brim full with samples.

2. After that we immediately add 2mL of manganese sulphate to the collection bottle by inserting the calibrated pipette just below the surface of the liquid. (If the reagent is added above the sample surface, we will introduce oxygen into the sample.) Then we squeeze the pipette slowly so that no bubbles are introduced via the pipette.

3. Similarly, we add 2 mL of alkali-iodide-azide reagent in the same manner.

4. Then we mix the sample by inverting the DO bottle several times. Checking for air bubbles is very necessary and if found then we discard the sample and start over. If oxygen is present, a brownish cloud of precipitate will appear. When this flock has settled to the bottom, we mix the sample by turning it upside down several times and let it settle again.

5. 2 mL of concentrated sulphuric acid is added via a pipette held just above the surface of the sample, then carefully stopper and invert several times to dissolve the flock. At this point, the sample is "fixed" and can be stored for up to 8 hours if kept in a cool, dark place.

6. In a glass flask, we titrate 200 mL of the sample with sodium thiosulfate to a pale straw colour. Then we titrate by slowly dropping titrant solution from a calibrated pipette into the flask and continually stirring or swirling the sample.

7. On completion of the previous steps, we add 2 mL of starch solution so a blue colour forms.

8. We continue slowly titrating until the sample turns clear. As this experiment reaches the endpoint, it will take only one drop of the titrant to eliminate the blue colour. We have to be especially careful that each drop is fully mixed into the sample before adding the next. It is sometimes helpful to hold the flask up to a white sheet of paper to check for the absence of the blue colour.

9. The concentration of dissolved oxygen in the sample is equivalent to the number of milliliters of titrant used which is called the azide modification of the wrinkle test. Each mL of sodium thiosulfate added in steps 6 and 8 equals 1 mg/L dissolved oxygen.

Location	DO
• Site 1	5.4
• Site 2	4.5
• Site 3	8.28
• Site 4	9.798
• Site 5	9.02

Table 4.3

4.4 TDS: Total dissolved solids are a measure of the dissolved combined content of all inorganic and organic substances present in a liquid in molecular, ionized, or micro-granular suspended form. TDS concentrations are often reported in parts per million.

Water TDS concentrations were determined using a digital meter. Maximum desires TDS is 50 - 150 mg.

Location	TDS
• Site 1	124
• Site 2	355
• Site 3	208.75
• Site 4	223.25
• Site 5	341.25

Table 4.4

4.5 BOD: In the presence of free oxygen, aerobic bacteria use the organic matter found in wastewater as "food". The BOD test is an estimate of the "food" available in the sample. The more "food" present in the waste, the more Dissolved Oxygen (DO) will be required. The BOD test measures the strength of the wastewater by measuring the amount of oxygen used by the bacteria as they stabilize the organic matter under controlled conditions of time and temperature.

BOD is to measure the amount of biologically oxidizable organic matter present in waste. BOD is a major criterion parameter in stream pollution control. The BOD shows higher concentration in the surface water than groundwater. A sample is pipetted into a BOD bottle containing aerated dilution water. The DO content is determined and recorded and the bottle is incubated in the dark for five days at 20°C. At the end of five days, the final DO content is determined and the difference between the final DO reading and the initial DO reading is calculated. The decrease in DO is corrected for

sample dilution, and represents the biochemical oxygen demand of the sample. The reagents used are: Potassium dihydrogen phosphate buffer (KH2PO4), Magnesium sulphate solution (MgSO4 7H2O), Dipotassium hydrogen phosphate (K_2HPO_4), Disodium hydrogen phosphate ($Na_2HPO_4.7H_2O$), Calcium chloride ($CaCl_2$), Ferric chloride ($FeCl_3$), Sodium hydroxide ($NaOH$) 1 N, Sulfuric acid (H_2SO_4) 1 N, Sodium thiosulfate ($Na_2S_2O_3$) 0.1N, Starch indicator solution, Distilled water.

The following steps are carried out to determine BOD:

1. We completely fill two BOD bottles with dilution water.
2. Then into additional BOD bottles, partially filled with dilution water, carefully measure out the proper volume of sample. Add dilution water until the bottles are completely filled.
3. The Stopper of each bottle is taken care to avoid trapping air bubbles inside the bottles as the bottle stoppers are inserted.
4. We Fill the top of each bottle neck around the stopper with dilution water.
5. And then we determine the initial DO content on one of each set of duplicate bottles, including the dilution water blank by one of the approved methods and record data on the lab sheet.
6. After which we place the remaining bottles in the incubator at 20°C and incubate for five days.
7. At the end of exactly five days (+/-3 hours), we test the DO content of the incubated bottles.
8. Calculation of the BOD for each dilution is done. The most accurate BOD will be obtained from those dilutions that have a depletion of at least 2 mg/L DO and at least 1.0 mg/L DO residual. If there is more than one dilution that meets these criteria, the BOD results should be averaged to obtain a final BOD value.

9. The dilution water blanks are used only to check the quality of the dilution water. If the quality of the water is good and free from impurities, the depletion of DO should be less than 0.2 mg/L. In any event, do not use the depletion obtained as a blank correction

Location	BOD
• Site 1	6.9
• Site 2	5.46
• Site 3	15.44
• Site 4	7.7
• Site 5	16.58

Table 4.5

4.6 COD: Chemical Oxygen Demand (COD) is a test that measures the amount of oxygen required to chemically oxidize the organic material and inorganic nutrients, such as Ammonia or Nitrate, present in water.

The organic matter and oxidizable inorganic substances present in water or wastewater get oxidized completely by standard potassium dichromate (K2Cr2O7) in the presence of sulphuric acid (H2SO4) to produce carbon dioxide (CO2) and water (H2O). The excess potassium dichromate (K2Cr2O7) remaining after the reaction is titrated with ferrous ammonium sulphate. The dichromate absorbed gives the O2 required for oxidation of the organic matter.

The contents are refluxed for 2 h. It is based on the principle that all organic compounds can be oxidized by strong oxidizing agents in acidic media. Throughout the experiment, excess dichromate concentration is determined by titrating it with ferrous ammonium sulphate (FAS).

The reaction is given by:

$$\mathbf{6Fe2 + Cr2O7^{2-} + 14\ H^{+} \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H2O}$$

The apparatus used are: COD Reflux apparatus consisting of a flat bottom 500-mL capacity flask with condenser and a heating mantle.

The chemical used are as follows:

1. Potassium dichromate, $K_2Cr_2O_7$.

2. Conc. sulphuric acid, H_2SO_4.

3. Sulphuric acid, H_2SO_4.

4. Silver sulphate, Ag_2SO_4.

5. Ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2.6H_2O$.

6. Mercuric sulphate, $HgSO_4$.

The following steps are used to determine COD:

1. Firstly, we take a 500 mL capacity flat-bottom conical flask and add 0.4 g of $HgSO_4$.

2. Then add 20 mL of sample or a liquor of sample diluted to 20 mL with distilled water and mix well.

3. After which we add a few glass beads followed by 10 mL of 0.025 Or 0.25 N potassium dichromate depending upon the expected COD.

4. Then we slowly add 30 mL conc. H_2SO_4 + Ag_2SO_4, reagent and mix thoroughly. The slow addition along with swirling prevents fatty acids from escaping due to high temperature.

5. We mix it well and if the colour is green, take either a fresh sample with lesser aliquot or add more dichromate and H_2SO_4. Connect the flask to the condenser and mix the contents before heating. Improper mixing will result in bumping and samples may be blown out.

6. Then we reflux for a minimum of 2 h after which we cool and then wash down the condenser with distilled water.

7. Finally, we dilute for a minimum of 150 ml. (about 300 mL), cool to room temperature and titrate excess $K_2Cr_2O_7$ remaining after refluxing with corresponding standard ferrous ammonium sulphate using ferroin as an indicator (8-10 drops). A sharp colour change from blue green to wine red indicates the end point or completion of the titration. Perform blank in the same manner using distilled water instead or sample

CALCULATION:

COD (mg/L) = (A-B) *N*g*100/ mL of the sample

Where, A= mL of ferrous ammonium sulphate used for blank

B= mL of ferrous ammonium sulphate used for the sample

N= Normality of ferrous ammonium sulphate

Location	COD
• Site 3	178.5
• Site 4	64.75
• Site 5	73.5

Table 4.6

4.7 Chloride test: Chloride occurs in all-natural water in widely varying water samples. Not harmful if concentration less than 250 mg/litre. It is measured by the Argentometric method. This method recommends the use of 0.0141N solution of silver nitrate for titration. 1ml of this silver nitrate solution is equivalent to 0.5 mg of chloride ion. In the titration the chloride ion is precipitated as white silver chloride.

Indicator normally used is Potassium chromate. Silver chromate as precipitate begins to form a reddish-brown precipitate.

Procedure:

1. Take a 100 ml sample in a beaker.
2. Adjust pH to 7 to 10 with $H2SO4$ or NaOH if not in range.
3. Add 1 ml Potassium chromate indicator.
4. Titrate with standard $AgNO3$ titrant to a pinkish yellow end point.
5. Standard $AgNO3$ titrant and establish reagent blank value by above method.

Calculations:

Mg Cl/L = (A – B) * N* 35450/volume of sample

Location	Chloride
• Site 1	15.9
• Site 2	21.4
• Site 3	49
• Site 4	17.39
• Site 5	20.96

Table 4.7

4.8 Hardness: Hardness in water is due to the presence of dissolved salts of calcium and magnesium. It is unfit for drinking, bathing, washing and it also forms scales in boilers. Hence it is necessary to estimate the amount of hardness producing substances present in the water sample. Once it is estimated, the amount of chemicals required for the treatment of water can be calculated. The estimation of hardness is based on complexometric titration. Hardness of water is determined by titrating with a standard solution of ethylene diamine tetra acetic acid (EDTA) which is a complexing agent. Since EDTA is insoluble in water, the disodium salt of EDTA is taken for this experiment. EDTA can form four or six coordination bonds with a metal ion. Two type of hardness is present in water first is temporary hardness and second is permanent hardness. Temporary hardness is due to the presence of bicarbonates of calcium and magnesium ions. It can be easily removed by boiling. Permanent hardness is due to the presence of chlorides and sulphates of calcium and magnesium ions. This type of hardness cannot be removed by boiling.

Reagents: EDTA, Eriochrome Black-T, NH2CL, Ammonia Buffer, Magnesium Carbonate, 90% ethyl alcohol, Distilled water.

Reagent preparation:

1. EDTA solution: 4gm EDTA and 0.1gm magnesium bicarbonate dissolve in 800 ml distilled water. 2. Eriochrome Black-T: 0.4gm Ericrome Black T, 4.5 gm hydroxylamine hydrochloride add in 100ml 95% ethyl alcohol.

3. Ammonia Buffer: Stock A: 16.9gm of NH4CL in 143ml of conc. NH4OH, Stock B: 1.25gm magnesium salt of EDTA dissolve in 50 ml distilled water. Mix both stock solutions and dilute to 250ml with DDW. Dilute 10ml of the solution to 100ml with DDW.

Procedure:

1. The burette is filled with standard EDTA solution to the zero level.
2. Take 50ml sample water in flask. If sample having high Calcium content, then take smaller volume and dilute to 50ml.
3. Add 1ml Ammonia buffer.
4. Add 5 to 6 drop of Ericrome black – T indicator. The solution turns into wine red colour.
5. Note the initial reading.
6. Titrate the content against EDTA solution. At the end point colour change from wine red to blue colour.

7. Note the final reading and record it. Repeat the process till we get concordant value.

8. Take 50ml sample in another flask and boiled it. (Add distilled water to get final volume of water.)

Location	Hardness
• Site 4	50.62
• Site 5	22.75

Table 4.8

4.9 TSS: Total suspended solids (TSS) are defined as solids in water that can be trapped by a filter. To measure TSS, the water sample is filtered through a pre-weighed filter. The residue retained on the filter is dried in an oven at 103–105°C until the weight of the filter no longer changes. The increase in weight of the filter represents the TSS.

Location	TSS
• Site 3	31.75
• Site 4	25.25
• Site 5	30

Table 4.9

CHAPTER 5

OBSERVATION

4.10 Tabular representation of various parameters at different location

Sites	Location	pH	Conductivity ((µS/cm)	DO (mg/L)	TDS	BOD (mg/L)	COD (mg/L)	Chloride	Hardness	TSS
Site 1	• Middle side	9	262	5.4	124	6.9	—	15.9	—	—
Site 2	• Middle side	9.2	458	4.5	355	5.46	—	21.4	—	—
Site 3	• Right side (Surface)	9.3	320	8.2	208	15.1	184	44	—	34
	(Depth of 1m)	9.1	368	8.1	118	17.2	192	48	—	33
	• Middle side (Surface)	8.2	420	8.5	249	13.85	162	51	—	29
	(Depth of 1 m)	8.4	472	8.3	260	15.62	176	53	—	31

Site 4	• Right side (Surface)	7.5	285	9.93	132	7.703	56	15.59	50.5	24
	(Depth of 1 m)	7.3	269	9.32	138	7.90	62	14.3	49.5	22
	• Middle side (Surface)	7.7	286	10.3	320	7.09	59	18.45	51.5	28
	(Depth of 1 m)	7.5	297	9.91	303	8.108	82	21.2	51	27
Site 5	• Right side (Surface)	7.9	258	7.9	320	18	84	22.69	22	26
	(Depth of 1 m)	7.8	283	8.11	335	17.5	69	21.3	23	29
	• Middle side (Surface)	7.3	317	10.39.	349	14.8	62	16.45	23.5	35
	(Depth of 1 m)	7.7	392	72	361	16	79	23.4	22.5	32

Deviations observed for the different parameters

Site - 3

PARAMETERS	RIGHT BANK		MIDDLE OF THE RIVER		Average Values	Deviation % (From WHO std.)
	Surface	**1m. Depth**	**Surface**	**1m. Depth**	**Overall Site**	**Overall Site**
pH.	9.31	9.18	8.22	8.14	8.71	+16.13
Conductivity	320 µs/cm	368 µs/cm	420 µs/cm	472 µs/cm	395	+31.67
TSS	34 mg/L	33 mg/L	29 mg/L	31 mg/L	31.75	-68.25
TDS.	208 mg/L	118 mg/L	249 mg/L	260 mg/L	208.75	+89.56
DO	8.2 mg/L	8.1 mg/L	8.5 mg/L	8.3 mg/L	8.28	+18.28
BOD	15.1 mg/L	17.2 mg/L	13.85 mg/L	15.62 mg/L	15.44	+208.8
COD.	184 mg/L	192 mg/L	162 mg/L	176 mg/L	178.5	+1685
Chloride.	44 mg/L	48 mg/L	51 mg/L	53 mg/L	49mg/L	-80.4

Table 4.11

- **WHO standard for different parameters of lake water:**

pH- 6.5-8.5; EC <300µs/cm; DO = 6-8 ppm; BOD < 5ppm; COD < 10ppm; TSS < 100ppm; TDS < 2000ppm; Hardness < 600ppm; Chloride = 200-300 ppm

- **"+" indicating more than the standard WHO parameter, "-"indicating less than the same in percentage**

Site – 4

PARAMETERS	**RIGHT BANK**		**MIDDLE OF THE RIVER**		**Average Values**	**Deviation % (From WHO std.)**
	Surface	**1m. Depth**	**Surface**	**1m. Depth**	**Overall Site**	**Overall Site**
Ph.	7.5	7.3	7.7	7.5	7.5	0
Conductivity	285µs/cm	269µs/cm	286µs/cm	297µs/cm	284.25	-5.25
TSS	24mg/L	22mg/L	28mg/L	27mg/L	25.25	-74.75
TDS.	132mg/L	138mg/L	320mg/L	303mg/L	223.25	-88.84
DO.	9.932mg/L	9.32mg/L	10.03 mg/L	9.91 mg/L	9.798	+39.97
BOD	7.703mg/L	7.90mg/L	7.09mg/L	8.108mg/L	7.7	+54
COD.	56mg/L	62mg/L	59mg/L	82mg/L	64.75	+547.5
Chloride.	15.59mg/L	14.3mg/L	18.45mg/L	21.2mg/L	17.39	-93
Hardness	50.5	49.5	51.5	51	50.62	-91.56

Table 4.12

Site - 5

PARAMETERS	RIGHT BANK		MIDDLE OF THE RIVER		Average Values	Deviation % (From WHO std.)
	Surface	1m. Depth	Surface	1m. Depth	Overall Site	Overall Site
pH.	7.9	7.8	7.3	7.7	7.68	+2.4
Conductivity	258µs/cm	283µs/cm	317µs/cm	392µs/cm	312.5µs/cm	+4.17
TSS	26mg/L	29mg/L	35mg/L	32mg/L	30mg/L	-70
TDS.	320mg/L	335mg/L	349mg/L	361mg/L	341.25	-82.94
DO	7.90mg/L	8.11mg/L	10.34 mg/L	9.72 mg/L	9.02	+28.85
BOD	18mg/L	17.5mg/L	14.8mg/L	16mg/L	16.58	+231.6
COD.	84mg/L	69mg/L	62mg/L	79mg/L	73.5	+635
Chloride.	22.69mg/L	21.3mg/L	16.45mg/L	23.4mg/L	20.96	-91.62
Hardness	22	23	23.5	22.5	22.75	-96.21

Table 4.13

CHAPTER 6

RESULT AND DISCUSSION

6.1 Result Analysis:

An analysis of the water quality data collected during 5 months between January 2023 to May, 2022 by students of Assam Engineering College revealed that the pH of the water collected from different sampling points across the Deepor Beel was between 7.68 to 9.2. The basic condition of the Deepor Beel is majorly due to the industrial waste generated by some industrial set-ups as it contains materials with carbonates, bicarbonates and hydro carbonates and their inflow of wastewater from the nearby industries. It was more basic in the zones 1, 2 and 3 since it was very near to the industrial site and the dumping zone, Boragaon. Zone 1 and 2 was not within the range recommended by WHO. The Conductivity of the water sample collected during the entire time ranged between 262 to 458 μS/cm. The high range of conductivity is related to total dissolved solids concentration in water, amount of dissolved mineral salts in water. All the values except for Zone 1 and 4 were above the permissible limt. The Dissolved Oxygen of the water was ranging from 5.4 to 9.02. For zone 1 and 2 it was lower because of the probable inflow from the industries and low living organisms such as plants and algae in the site, whereas in zone 4 and 5 plants were in a reasonable amount which could add in the increase in DO levels. The BOD of the Deepor Beel during the entire period of sampling was reported to be ranging between 5.46 to 16.58 mg/L which shows that it is moderate to highly polluted which means that there is a scope for vegetation if the wastewater is treated. The COD values were also very high ranging between 64.75 mg/L to 178.5 mg/L which is very much more than the permitted value recommended by WHO. The high BOD and COD values indicate the very high level of industrial and domestic pollution of the Deepor Beel.

GRAPHS AND HISTOGRAM

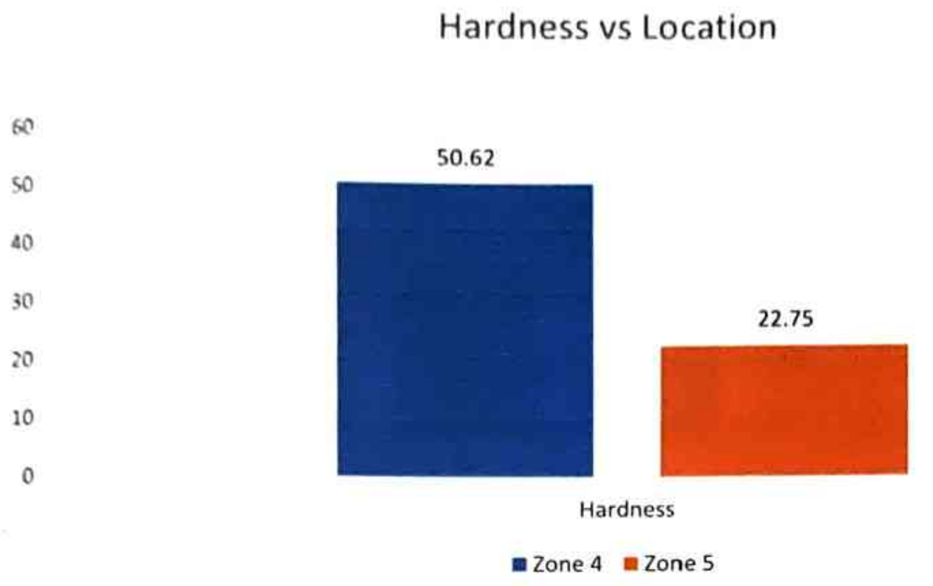

Fig 2: Graphs comparing the average Hardness Levels for the respective locations in a single histogram.

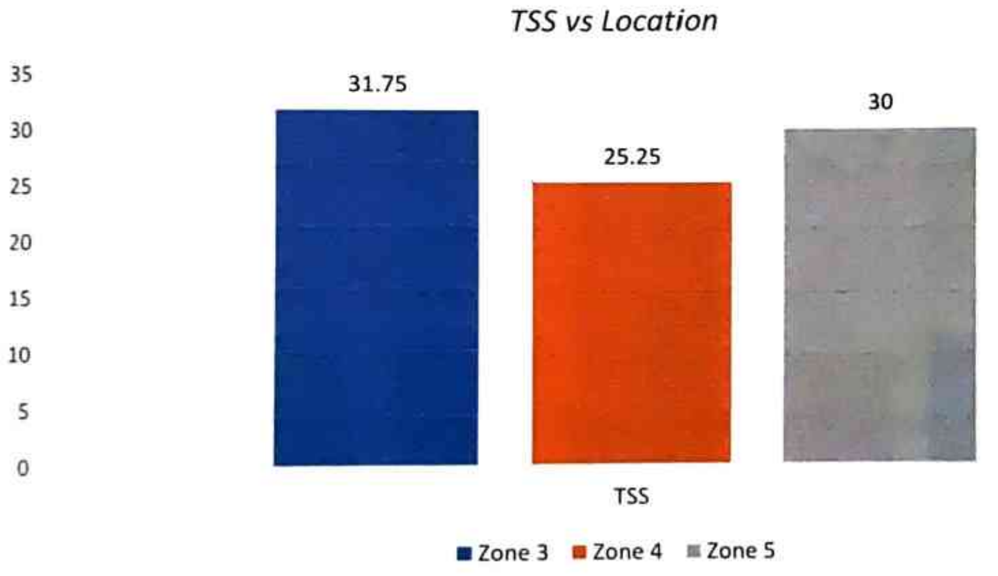

Fig 3: Graphs comparing the average TSS Levels for the respective locations in a single histogram.

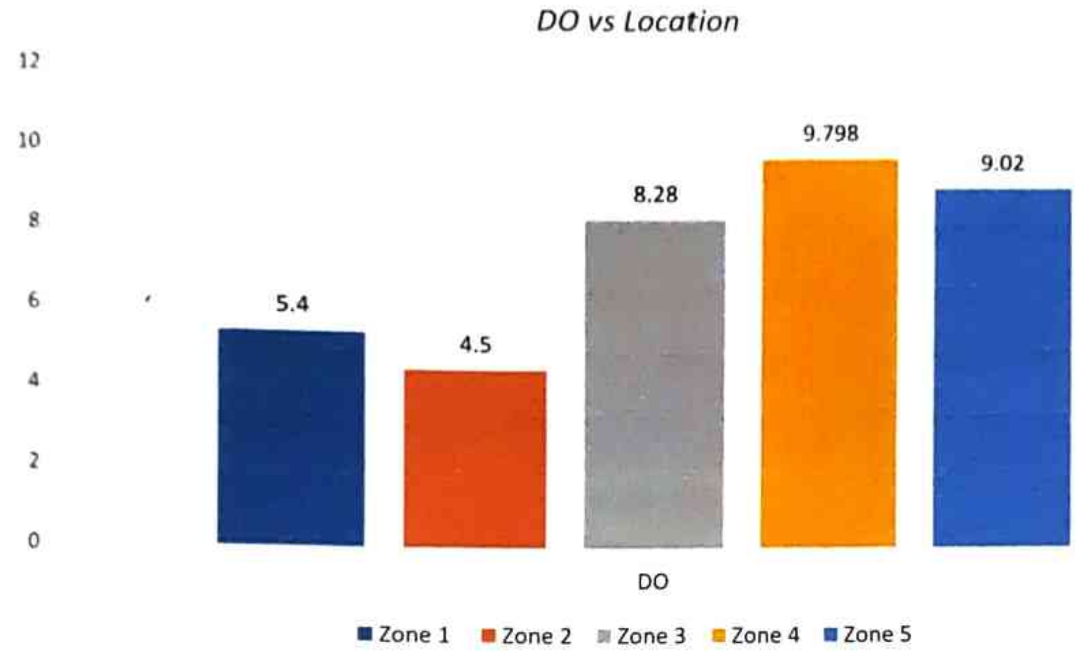

Fig 4: Graphs comparing the average DO for the respective locations in a single histogram.

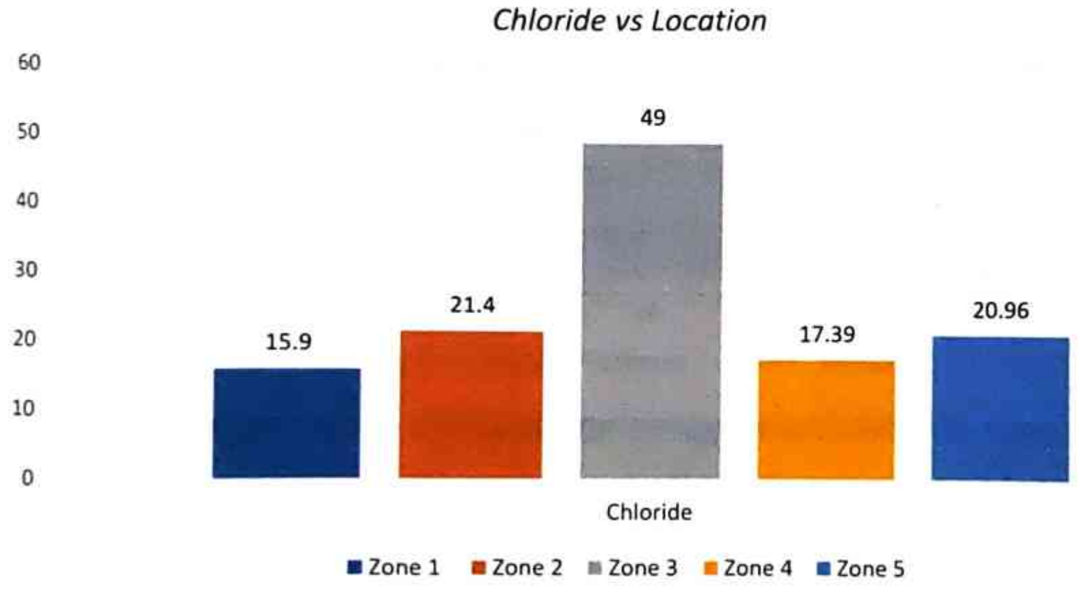

Fig 5: Graphs comparing the average Chloride level for the respective locations in a single histogram.

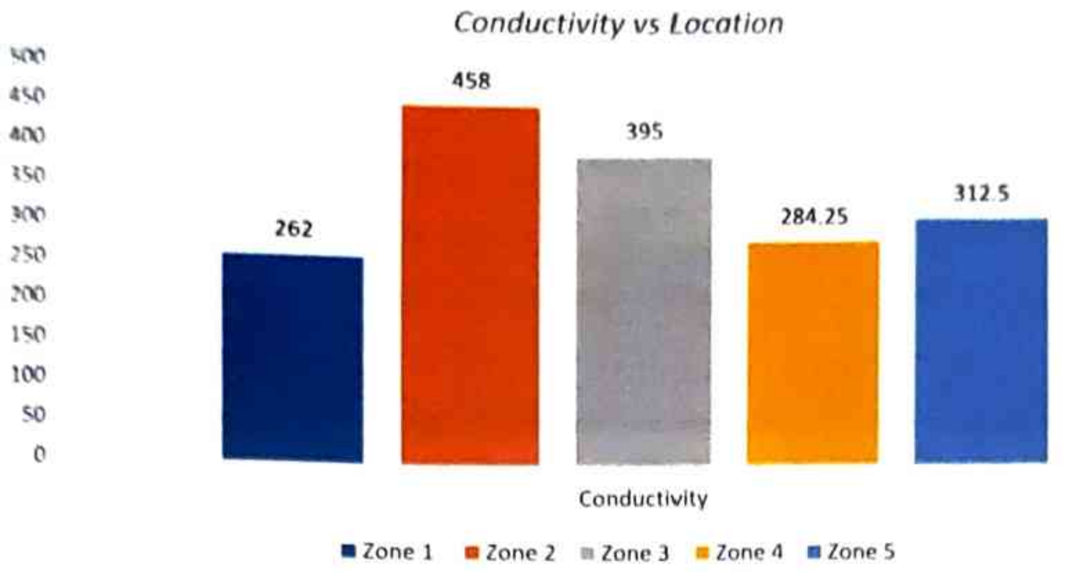

Fig 6: Graphs comparing the average Conductivity level for the respective locations in a single histogram.

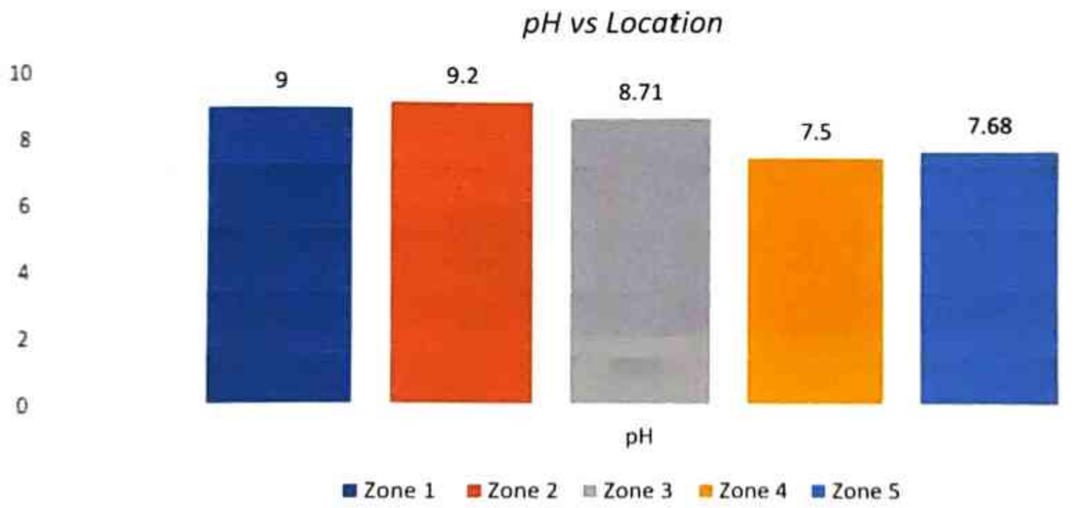

Fig 7: Graphs comparing the average pH for the respective locations in a single histogram.

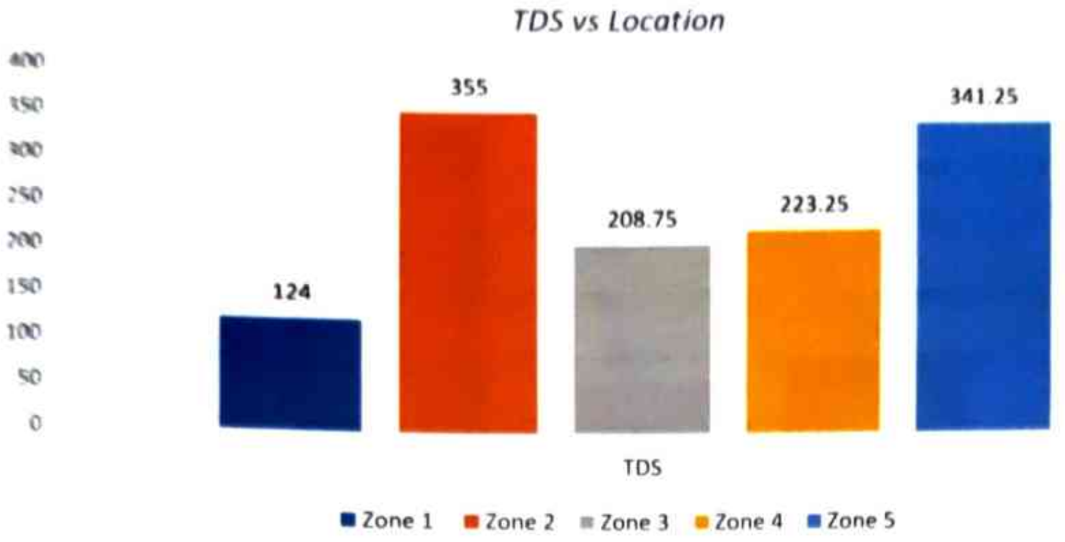

Fig 8: Graphs comparing the average TDS content for the respective locations in a single histogram.

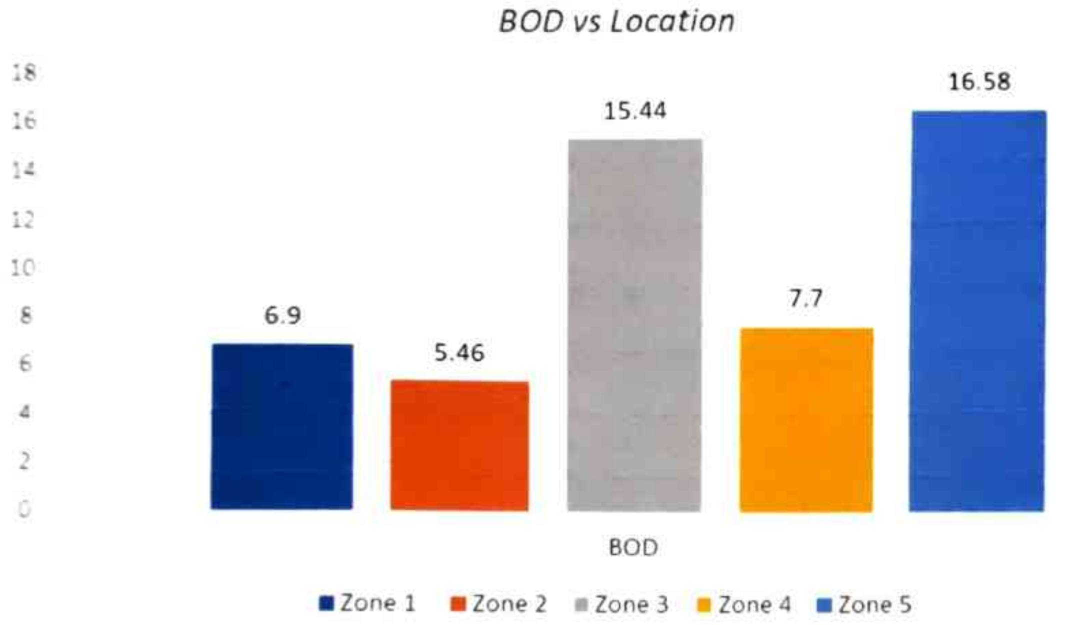

Fig 9: Graphs comparing the average BOD content for the respective locations in a single histogram.

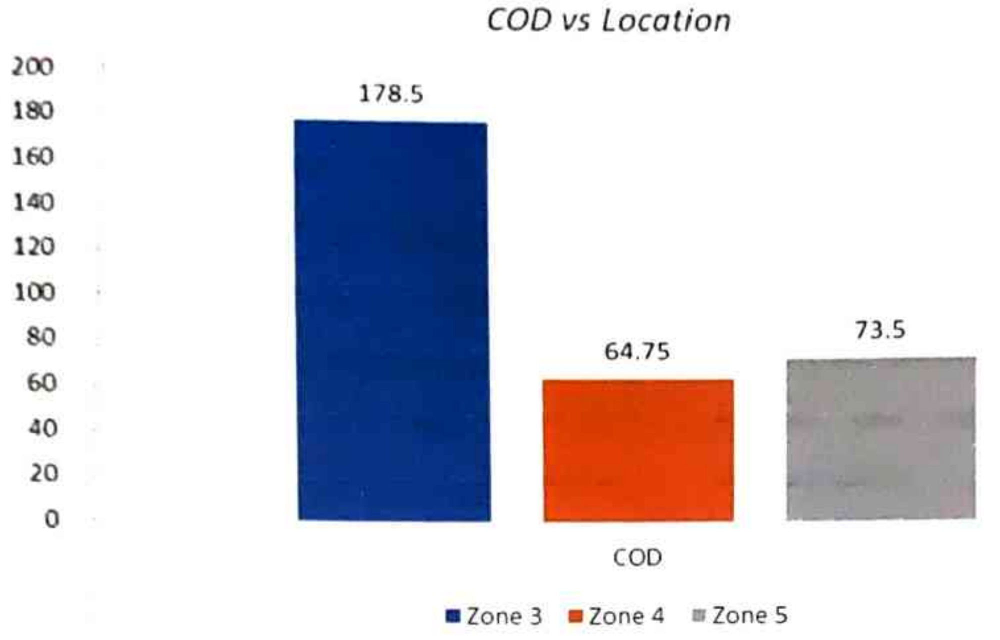

Fig 10: Graphs comparing the average Conductivity level for the respective locations in a single histogram.

6.2 MANAGEMENT OF INDUSTRIAL, MUNICIPAL AND PLASTIC WASTE

Tabular representation of types of waste and their status

Sl. No	Type	Status	Proposed actions	Authority
1	**Industrial Waste**	➢ Authorization have been granted to different industries in line with Water act 1974 Hazardous Waste Rule, 2008. ➢ Regular monitoringby PCBA	➢ Direction issued to the industries to identify the non-point sources and arrest contamination of water. ➢ Directions to be issued to the defaulter units.	Pollution Control Board Assam
2	**Municipal solid waste**	➢ Guwahati Municipal Corporation has engaged NGOs ward wise for collection of Municipal Solid Waste from the generation source itself. ➢ The wastes are being segregated into dry and wet waste categories and are collected separately.	➢ Directions have been issued by Pollution control Board, Assam ➢ Formation of City Sanitation task Force ➢ Door-to-door garbage Collection of waste	Guwahati Municipal Corporation

3	**Plastic Waste**	➢ Dumping is carried out unscientifically in the open space along with the municipal waste. ➢ No proper segregation of bio- degradable and non- biodegradable waste ➢ No proper segregation of dry and wet waste ➢ Lack of scientific disposal facilities/infrastructure technology like decentralized composting or bio-methanation plant, waste to energy plant, solid waste management plant.	➢ Issue directions to Municipal Board to segregate and collect plastic waste and initiate necessary steps to channelize the waste to authorized agencies for recycling reprocessing	Guwahati Municipal Corporation /Pollution Control Board Assam

Table 4.14

6.3 REMEDIES AND SUGGESTION

PREVENTIVE METHODS (Indirect Method): This are the methods which identify the pollutants, reduce their rate of generation and prevent them from reaching the lake.

1. Drainage Basin Alterations:

This approach is useful primarily for controlling non - point sources of pollution which are incidental to the land use of the drainage basin of the lake. Land development activities, logging of forest and other construction activities increases soil erosion and thus sediment runoff. Phosphorus and nitrogen from the fertilizer used in farming operations are transported with the sediments.

The drainage basin alterations involve structural and land treatment measures and interception of nutrients and sediments before they reach the lake. The main soil erosion management practices like Grassed waterways, crop residue management and creation of shelters belts can be beneficial to some extent.

2.Diversion of Waste:

This is a frequently used solution for improving the water quality of eutrophic lakes. Before undertaking this method, it is necessary to account for all the sources of nutrients to the lake so that the impact of diverted nutrients sources can be estimated. This solution is reasonable if the wastewater is mainly of domestic origin, the ecosystem receiving the waste is able to maintain the balance and there is enough water in the former ecosystem to bear the loss . Otherwise, the diverted wastewater can be treated.

AMELIORATIVE METHODS - (DIRECT METHODS)

This are the methods which involve either the treatment of the waste before discharge into the lake (outside lake methods) or direct intervention in the lake (in Lake methods).

1. PHYSICAL METHODS:

   MECHANICAL HARVESTING OF BIOMASS: Harvesting of biomass may be useful if the rate of removal by existing machinery can be improved making it an economical alternative. Some beneficial use of harvested material is yet to be found as an aid to reduce operating costs.

2. ADMISSION OF UNPOLLUTED WATER (DILUTION / FLUSHING)

   Admission of water or dilution results lowering of nutrients concentration and a washout of algal cells, whereas flushing achieves only a washout of algal cells. The effectiveness of this restoration technique increases with an increase in the difference between nutrient concentration in the inflow and lake water. The method will be economical if an adequate supply of good quality water exists and the costs of facilities and their maintenance for delivering the water to the lake are not high.

3. AERATION OF WATER: Dissolved oxygen (DO)is very low in deep waters of stratified lakes during summer. The DO is needed by all the living organisms in the lake for their survival. The DO deficiency occurs mainly because of the decomposition of organic material in the hypolimnion and thermal stratification which restricts movement of cold, dense water in the hypolimnion to the overlying waters in the metalimnion and epilimnion. When the DO levels fall close to zero, more phosphorus is released from the sediments under the prevailing anaerobic conditions. This causes algal blooms, which produce more organic matter, requiring more dissolved oxygen. One ameliorative technique is to pump hypolimnetic water to the surface and allow it to mix with warm epilmnetic water, or force the epilimnetic water to the hypolimnion. The resulting mixing and disruption of the thermal stratification improve the DO in the deeper waters at the expense of the shallower waters. The other technique is to directly aerate the hypolimnetic water.

4. HYPOLIMNETIC DRAINAGE: In a thermally stratified lake, the cool and stagnant bottom layer (hypolimnion) is rich in nutrients and low in dissolved oxygen whereas the upper warmer layer (epilimnion) has fewer nutrients and high dissolved oxygen. By the withdrawal of water from the bottom layers instead of from the top, the nutrients in the lake are reduced and the dissolved oxygen condition can be improved.

IN LAKE CHEMICAL METHODS:

1. PHOSPHORUS PRECIPITATION: This method involves successive applications of aluminum sulfate or alum to disrupt the internal phosphorus cycle. This method can be helpful in decreasing phosphorus levels and eliminating nuisance algal growth and increasing water clarity.

2. USE OF ALGICIDES: Chemical treatments have been used for control of nuisance algal blooms and dense growth of macrophytes. Copper sulfate has been widely used for control of blue-green algae.

3. USE OF SODIUM HYDRGEN CARBONATE STREAMS RUN OFF: This method is useful in reducing ph.

IN LAKE BIOLOGICAL METHODS:

1.Species manipulation is the main in-lake biological method for lake restoration. The method considers the introduction or promotion of organisms that are inimical to the target organisms. In nature, predation by zooplankton and fish species keeps a sort of control on algal populations.

OUTSIDE LAKE PHYSICAL METHODS:

MECHANICAL TREATMENT: Such a treatment was patented for removing water soluble substances from the rainwater runoff. Magnetically attractable collection units containing an ion-exchange or sorbent medium with an affinity for a chosen target substance are distributed in the sediments. After a period of time has passed sufficient for the particles to bind up the target substances, a magnet drawn through the sediments or across the tailings retrieves the units along with the target substances. In many cases this medium can be regenerated and the units subsequently put back into use.

OUTSIDE LAKE CHEMICAL METHODS:

1. CLARIFICATION: Chemical clarification, properly conducted, transforms raw wastewater to a fully clarified effluent with substantially reduced concentrations of phosphorus, organic matter and metals. The clarifying agents used are Fe Cl3, lime, and alum. Clarification typically removes 70-80 percent of organic matter, 90-98 percent of suspended solids, and 80-98 percent of phosphorus. The weight of sludge produced is increased considerably because of the greater removal of suspended solids and because of the presence of precipitated hydroxides, carbonates, and phosphates.

2. ACTIVATED CARBON ADSORPTION: Activated carbon is a generic term for a broad range of amorphous carbon-based materials so prepared as to exhibit a high degree of porosity and an extensive associated surface area. The concept of applying clarification and sorption processes directly to raw wastewater rather than to secondary effluents is derived from effectiveness and reliability of treatment and from economic considerations. An organic removal of about 95 percent or more is achieved. In the most common type of adsorber system, the effluent is passed through fixed beds of granular carbon. For backwashing, it is advisable to include a surface wash and air scour to be assured of removing suspended solids as well as gelatinous biologic growth.

3. DISINFECTION: Chlorine is both efficient and reasonably cheap for disinfecting effluents. Ozone is efficient but relatively expensive. Chlorine inactivates enzymes that are essential to the metabolic process of bacterial cells. Chlorination of sewage can be thought of as a two-stage process, addition of sufficient chlorine for satisfaction of chlorine demand and further addition of chlorine for maintenance of free chlorine. The rate of disinfection is a function of the time of contact, the concentration of the disinfectant, and the temperature of the water. Chlorination for lowering the BOD of wastewater effluents has been practiced to control nuisance conditions in a receiving stream during drought flows.

OUTSIDE LAKE BIOLOGICAL METHODS:

Primary treatment of sewage is achieved with plain sedimentation. The fresh solids contain most of the settleable solids in the raw wastewater. An aerobic digestion destroys about 67 percent of the volatile matter, and about a quarter of it is converted to fixed solids. The secondary treatment includes trickling filters and activated sludge. Various removal efficiencies are attained, such as about 85 percent for BOD, 80 percent for suspended solids, 90 percent for bacteria, and 70 percent for COD. Efficiencies drop when treatment plants are overloaded.

Advanced waste treatment methods and processes remove more contaminants from wastewater than are usually taken out by conventional secondary treatment plants. An example is the chemical addition in the activated-sludge biological process to precipitate phosphorus. Some advanced waste-treatment processes are biologic. Biological nitrification and denitrification in association with activated sludge process can greatly reduce water quality problems in a lake.

CHAPTER 7

SURVEYS CONDUCTED

A total of 50 Surveys were conducted through questionnaire in Zone 3, 4 and 5. A brief summary has been presented for all the three zones which was concluded from the surveys.

SURVEY REPORT ANALYSIS FOR ZONE -3

1. Areas Visited – **Pamohi**

2. Duration of people staying in those areas – **2 - 10 years**

3. Changes that have been noticed: -
    - The quantity of fish **has reduced**
    - The water has been **polluted**
    - Quantity of migratory birds **reduced**
    - Quality of the water **has decreased**

4. Advantages and disadvantages of staying near Deepor Beel: -

    Advantages: -
    - Different species of **Migratory Birds can be seen**
    - **Fresh Air**
    - **Different types of fish found**

    Disadvantages: -
    - Pollution **has increased**

5. Seasonal changes in fish
    - There have been some seasonal **changes in these types of fish (xingi, puthi etc.)**

SURVEY REPORT ANALYSIS FOR ZONE -4

1. Areas Visited – Surajnagar, near ASTU

2. Duration of people staying in those areas – 2 –20 years

3. Changes that have been noticed: -
    - The quantity of fish has reduced
    - The water has been polluted
    - Quality of the water has decreased
    - Water level of Deepor Beel has decreased
    - Foul smell is observed in the fish as well in Deepor Beel water.

4 Advantages and disadvantages of staying near Deepor Beel: -

Advantages: -
- Fresh Air
- Various species of fish found

Disadvantages: -
- Pollution has increased
- Flood prone area
- Death of cattle during flood
- No proper road near Deepor Beel

Seasonal changes in fishes (kawoi, magur, xingi, etc)

SURVEY REPORT ANALYSIS FOR ZONE -5

1. Areas Visited – Madhuapara, MoloyNagar

2. Duration of people staying in those areas – 3 – 40 years

3. Changes that have been noticed: -
- The quantity of fish has reduced
- The water has been polluted
- Quantity of migratory birds reduced
- Quality of the water has decreased
- Air pollution has increased due to the Dumping Area
-

4. Advantages and disadvantages of staying near Deepor Beel: -

Advantages: -
- Different species of Migratory Birds can be seen
- Fresh Air
- Different types of fish found

Disadvantages: -
- Noise from the dumpers
- Pollution has increases
- Cattles avoiding to drink Deepor Beel water

5. Seasonal changes in fish: -

There have been some seasonal changes in these types of fish – Kawoi, magur, xingi, puthi.

CHAPTER 8

CONCLUSION

Sources of pollution identified till the submission of the report indicate that the main cause of pollution in the catchment area is anthropogenic causes and one of the major reasons behind this is lack of awareness among the common mass. Lack of government concern and policy for the Deepor Beel environment is also another cause and hence proper steps must be taken for the restoration of the lake environment which if not maintained will lead to serious imbalances in the environment. High amount of pollution has already led to the disappearance of important flora and fauna along the banks within a very short time span hence appropriate measures need to be taken to preserve the remaining ecological community.

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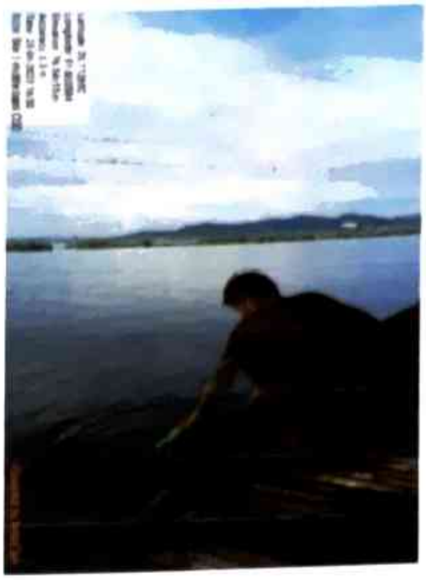
PHOTO GALLERY

SAMPLES COLLECTED: -



TESTS CONDUCTED FOR THE PARAMETERS: -

INDUSTRIES VISITED: -

SURVEYS CONDUCTED: -

FABRICATION AND CHARACTERIZATION OF CERAMIC MEMBRANE FOR WASTE WATER TREATEMENT

Submitted in partial fulfillment of

The requirement for Degree of

BACHELOR OF TECHNOLOGY

In

CHEMICAL ENGINEERING

Of

ASSAM SCIENCE AND TECHNOLOGY UNIVERSITY

SUBMITTED BY:

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B.Tech 8th SEMESTER

DEPARTMENT OF CHEMICAL ENGINEERING

ASSAM ENGINEERING COLLEGE

JALUKBARI GUWAHATI -13

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JALUKBARI GUWAHATI -13

JUNE 2023

Certificate

This is to certify that Nekib Javed (19254) , Ayushman Bhuyan (19272), Debabrata Das (19285) of B.Tech. 8th semester have jointly carried out the project entitled " **Fabrication and Characterization of Ceramic Membrane for Waste Water Treatment"** under my supervision and submitted the report in partial fulfillment of the requirement for the degree of Bachelor of Technology in Chemical Engineering which may be accepted.

04/07/2023

Dr. Ashim Kumar Basumatary

Project Guide

Associate Professor

Department of Chemical Engineering

Assam Engineering College

Acknowledgement

First & foremost, we would like to take an opportunity to extend our heartfelt gratitude to our respected Dr. Bandana Chakrabarty, Head of Department of Chemical Engineering of Assam Engineering College for providing us the opportunity to carry out our 8th semester project work.

We would also like to thank our respected project guide, Dr. Ashim Kumar Basumatary for his relentless support and guidance through the entire duration of the project work. Without his assistance, it would not have been possible to complete our project work successfully.

Last but not least, we would like to thank our lab assistants that have helped us in many ways.

Nekib Javed (19254)
Ayushman Bhuyan (19272)
Debabrata Das (19285)

DECLARATION

We,

Nekib Javed (19254)

Ayushman Bhuyan (19272)

Debabrata Das (19285)

Sincerely declare that the project report titled "**Fabrication and Characterization of Ceramic Membrane for Waste Water Treatment**" under the guidance of **Dr. Ashim Kumar Basumatary** is submitted to the **Department of Chemical Engineering , Assam Engineering College** in partial fulfillment of the requirements for the award of Bachelor of Technology degree in Chemical Engineering from Assam Engineering College.

We declare that this project has not been published previously elsewhere and is result of our own efforts and has been taken solely for the academic purpose. All educational materials consulted in the course of study have been declared in the reference and all information provided in the project is true and correct to the best of our knowledge.

Nekib Javed

Date:

1. Nekib Javed

Place:

Ayushman Bhuyan

2. Ayushman Bhuyan

Debabrata Das

3. Debabrata Das

PROJECT AT A GLANCE

Membrane technology plays a crucial role in contemporary society by facilitating separation processes in various domains, including water purification and fluid filtration. This project aims to elucidate the fabrication process of a tubular ceramic membrane utilizing an Extruder and inexpensive clay materials such as Kaolin, Feldspar, Quartz, CaCO3, Boric Acid, and carboxymethyl cellulose. The raw materials were meticulously mixed and transformed into a paste with the aid of milli-pore water. Subsequently, the paste was introduced into the extruder, resulting in the generation of tubular-shaped membranes, which were then allowed to dry at ambient temperature for 24 hours.The dried membranes were subjected to a sintering process, wherein they were gradually heated to 950° C at a rate of 0.5° C per minute. The sintering process consisted of three cycles: the first cycle involved heating from room temperature to 100° C, maintaining this temperature for 24 hours; the second cycle involved heating from 100° C to 200° C, followed by another 24 hour duration at 200° C; the third cycle encompassed heating from 200° C to 950° C and holding the membranes at 950° C for 6 hours. These stepwise heating procedures were executed using a muffle furnace.To evaluate the performance of the ceramic membrane, water flux tests were conducted to determine its permeability and pore size. Additionally, the filtered water was assessed for chemical oxygen demand (COD) and biochemical oxygen demand (BOD), while the membrane's porosity was also determined. This research demonstrates the potential of ceramic membranes as an efficient means of treating wastewater.

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CHAPTER 1

1.1 INTRODUCTION

Ceramic membranes are thin, porous filters made from ceramic materials that are used to separate and purify liquids, gases, and other substances. They are known for their high temperature resistance, chemical stability, and mechanical strength, making them suitable for use in a variety of filtration and separation applications. Ceramic membranes are often used in the food and beverage industry, as well as in the pharmaceutical, chemical, and petrochemical industries, among others. They can be used to filter and purify a wide range of substances, including water, juices, milk, beer, wine, and other liquids, as well as gases such as air and hydrogen. Ceramic membranes are generally more expensive to produce than other types of membranes, but they offer several benefits, including a long lifespan and the ability to operate at high pressures and temperatures

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1.1.1 USES

1. **Water Filtration**: Ceramic membranes are widely used in water treatment systems to remove impurities, bacteria, viruses, and other contaminants. The fine pores of ceramic membranes act as a physical barrier, allowing water molecules to pass through while blocking the passage of particles and microorganisms.

2. **Wastewater Treatment**: Ceramic membranes are crucial in wastewater treatment plants to separate solids, bacteria, and other pollutants from the water. By utilizing ceramic membranes, the treated water can be reused for various purposes or safely discharged into the environment.

3. **Oil/Water Separation**: Ceramic membranes are effective in separating oil and water mixtures, making them valuable in scenarios such as oil spills or industrial wastewater containing oil residues. The membranes can selectively allow water to pass through while retaining oil droplets, enabling the separation of these two liquids.

4. Microfiltration: Ceramic membranes with fine pore sizes are used for microfiltration applications. Microfiltration involves removing suspended solids, bacteria, and colloidal particles from various liquids, such as in beverage processing, pharmaceutical manufacturing, and water treatment.

5. Ultrafiltration: Ceramic membranes are also utilized for ultrafiltration processes. Ultrafiltration involves the removal of larger molecules, proteins, and macromolecules from liquids. This technique is commonly employed in protein concentration, enzyme purification, and the removal of pathogens from water.

6. Nanofiltration: Ceramic membranes with smaller pore sizes are employed for nanofiltration, which involves the removal of multivalent ions, organic compounds, and certain salts from water or other liquids. Nanofiltration is particularly useful in water softening, desalination, and the treatment of industrial effluents.

7. Gas Separation: Ceramic membranes can selectively separate gases based on their molecular size and permeability. This property finds applications in natural gas purification, hydrogen production, and carbon dioxide capture. By using ceramic membranes, specific gases can be separated from mixed gas streams efficiently.

8. Biotechnology: Ceramic membranes play a vital role in biotechnology processes. They are used for cell separation, cell culture, and various filtration and purification steps in the production of pharmaceuticals and bioproducts. Ceramic membranes help in isolating specific cell types, clarifying cell culture media, and purifying biopharmaceutical products.

9. Food and Beverage Processing: Ceramic membranes are employed in the food and beverage industry for clarification, sterilization, and concentration processes. They are used to remove particles, microorganisms, and unwanted components, ensuring the quality and safety of the final products.

10. Chemical Processing: Ceramic membranes find applications in chemical processing, including solvent recovery, purification of chemical streams, and separation of valuable chemicals from complex mixtures. These membranes can efficiently separate different chemical components based on their size and molecular properties.

11. **Catalysis**: Ceramic membranes with catalytic coatings are used in chemical reactions to enhance reaction rates, selectivity, and efficiency. The continuous separation of reaction products by the membrane allows for better control of the reaction and facilitates the recovery of desired products.

12. **Fuel Cells:** Ceramic membranes are essential components in solid oxide fuel cells. They separate oxygen ions from other gases and provide a pathway for the generation of electricity from fuels. Ceramic membranes contribute to the high efficiency and long-term stability of fuel cell systems.

13. **Metal Recovery**: Ceramic membranes are utilized in the mining and metallurgical industries for the recovery of valuable metals from process streams or the treatment of wastewater containing metal ions. These membranes allow the selective separation and concentration of target metals, aiding in resource recovery and reducing environmental impact.

14. **Semiconductor Industry**: Ceramic membranes are used in the semiconductor manufacturing process for the filtration and purification of ultrapure water. The semiconductor industry requires extremely high-quality water to ensure the reliability and performance of electronic components. Ceramic membranes play a critical role in removing impurities and contaminants from the water used in various manufacturing steps.

15. **Pharmaceutical Industry**: Ceramic membranes find applications in pharmaceutical manufacturing for the purification and concentration of drug solutions. They are also used for the removal of impurities and particulates from pharmaceutical products, ensuring product quality and safety.

These detailed explanations highlight the diverse applications of ceramic membranes across various industries, showcasing their versatility and importance in numerous filtration and separation processes.

1.2 PROPERTIES

Ceramic membranes are known for their high temperature resistance, chemical stability, and mechanical strength. Some other properties of ceramic membranes include:

1. **Chemical Stability**: Ceramic membranes exhibit excellent chemical stability, allowing them to withstand a wide range of chemical environments without degradation. They are resistant to acids, bases, and organic solvents, making them suitable for applications in aggressive chemical processes.

2. **Thermal Stability**: Ceramic membranes possess high thermal stability, enabling their use in processes involving elevated temperatures. They can withstand temperatures well above 1000°C without significant structural damage or loss of performance.

3. **Mechanical Strength:** Ceramic membranes are known for their high mechanical strength and rigidity. They can withstand high pressure differentials and mechanical stress without deformation or failure, making them suitable for applications that require robust and durable membranes.

4. **Pore Size Control:** Ceramic membranes can be precisely engineered to have specific pore sizes, ranging from microfiltration to nanofiltration. This allows for accurate control over the filtration and separation characteristics of the membrane, making them suitable for a wide range of applications with varying requirements.

5. **Selectivity:** Ceramic membranes can exhibit high selectivity towards certain molecules or particles based on their size, charge, or chemical properties. This selectivity enables them to separate and concentrate specific components from complex mixtures with high efficiency.

6. **High Flux Rates**: Ceramic membranes have high permeability and can achieve high flux rates, allowing for efficient and rapid filtration or separation processes. This property is particularly advantageous in applications where high throughput or productivity is desired.

7. Fouling Resistance: Ceramic membranes have inherent fouling resistance due to their smooth and hydrophilic surface properties. They are less prone to fouling by suspended solids, bacteria, and organic matter, resulting in longer operational lifetimes and reduced maintenance requirements.

8. Long Lifespan: Ceramic membranes are known for their exceptional durability and longevity. They can withstand prolonged use without significant deterioration in performance, making them cost-effective solutions in industrial processes that require continuous or extended operation.

9. Resistance to Abrasion: Ceramic membranes exhibit high resistance to abrasion and wear, allowing them to maintain their filtration properties even in harsh and abrasive conditions. This property is particularly beneficial in applications involving the filtration of abrasive slurries or chemically aggressive fluids.

10. Hydrophilicity: Ceramic membranes typically have hydrophilic surfaces, meaning they have a strong affinity for water. This property promotes the efficient passage of water through the membrane while minimizing fouling by enhancing the removal of waterborne contaminants.

11. Chemical Inertness: Ceramic membranes are chemically inert, meaning they do not react or interact with the substances being filtered or separated. This property ensures that the membrane does not introduce contaminants or alter the chemical composition of the process stream, maintaining the integrity of the desired product.

12. Low Extractables: Ceramic membranes have low levels of extractables, meaning they release minimal amounts of substances into the filtrate or separated components. This is crucial in applications where product purity is paramount, such as in the pharmaceutical or food industries.

13. Easy Cleaning: Ceramic membranes are relatively easy to clean due to their smooth and nonporous surface properties. Fouling can often be removed through simple backwashing or chemical cleaning methods, allowing for efficient membrane maintenance and restoration of performance.

14. Wide pH Range Compatibility: Ceramic membranes exhibit excellent pH stability and can tolerate a wide range of pH values, from highly acidic to highly alkaline conditions. This broad compatibility makes them suitable for applications in various industries, including those involving extreme pH environments.

15. Resistance to High Salinity: Ceramic membranes can withstand high salt concentrations without significant loss of performance. This property makes them suitable for desalination processes, as well as applications involving the filtration or separation of saline solutions or brines.

These detailed explanations highlight the key properties of ceramic membranes that contribute to their effectiveness and versatility in a wide range.

CHAPTER 2

Before proceeding towards the project, multiple surveys are needed to be done in order to learn about the advancements and developments. For carrying out the experiment, we performed various study and surveys which are stated below

2.1 Literature Survey

B.K. Nandi and R. Uppalur [1] in "Preparation and characterization of low cost ceramic membranes for micro-filtration applications" found that porosity decreases from 42% to 32% when sintering temperature is increased from 850°C to 1000°C . Pore size was found 5 Micro Meter and mechanical strength was found to be 3 to 8 MPa. Siti Khadijiah et. Al. [3] In "Fabrication and application of low cost ceramic membrane from kaolin" explained why kaolin is preferred for the preparation of low cost ceramic membrane instead of other clays such as ball clay. They found that kaolin has some very specific properties such as crystal order , chemical composition, mineralogical properties etc.It is generally free from impurities like iron and other minerals that allow higher flow rate of fluid and gases. Also kaolin is more stable than other clay at higher temperature. Fabrication and Optimization of a Clay-bonded SiC flat tubular membrane support for microfiltration application by Syed Zaighum , Jang-Hoon Ha et. Al. Here they have sintered the ceramic membrane at 1200 to 1500° C. The results show that a membrane with a smallsized starting powder, compared to a membrane with large-sized starting powder, has a high open porosity and high strength with a smaller pore size. The suggested optimum sintering temperature for the S-SiC, M-SiC and C-SiC samples was 1400°C. At this temperature, for CSiC, they achieved a 32.72 MPa flexural strength with 44% porosity and a pore size of 3.44 μm, whereas for M-SiC, they achieved a 45.93 MPa flexural strength with 47% porosity and pore size of 1.80 μm, and for S-SiC, they have achieved a 42 MPa flexural strength with 50% porosity and a pore size of 1.45 μm. It gives a roadmap for development and applications of ceramic membranes for liquid filtration. Rahim et all worked on the preparation and characterization of ceramic membrane using palm fibres pore forming agent. The membranes are characterized by various methods in order to determine its properties. The amount of porosity in ceramic membrane was increased from 36% to 54% with increasing amount of addition of palm fibres from 0 to 40 wt %. Amount of pore forming agent greatly influenced the properties of ceramic membrane. The porosity was increased with increasing amount of palm fibre, vice versa for density and compressive strength. Due to high porosity over 40% these ceramic membranes are highly potential to be used for filtration test. B.D.Bhide and S.A.Stern [5] gives an idea that cost evaluation is an important perspective to validate the viability of such membranes compared to those which are available in the market. Industrially applicable polymeric membranes cost around 50–200$ m^{-2} whereas, inorganic membranes are claimed to be more expensive such as 500–1000$ m^{-2}. So the cost prediction for preparing low cost membrane is very useful. Zularisam, A. W., Ismail, A. F., & Salim, M. R. (2012) in "Preparation and characterization of ceramic membranes for water and waste water applications: A critical review". provided a critical review of the preparation and characterization of ceramic membranes specifically for water and wastewater applications and also discussed various aspects of ceramic membrane fabrication, including the choice of raw materials, membrane forming techniques, and sintering processes.They have found that the systematic review of the existing literature, ceramic membrane is superior to polymeric membrane in terms of useful life span, permeate flux, fouling propensity, cleaning efficiency, and environmental impacts. Linares, R. V., & Tritz, W. J. (2019). [6] in "Ceramic membranes for water and wastewater treatment: A critical review; Journal of Water Process Engineering, 30, 100605" discussed the fabrication techniques employed in the production of ceramic membranes, highlighting different methods such as extrusion, tape casting, and phase inversion.It also discusses the properties of ceramic membranes, such as pore size distribution, permeability, selectivity, and mechanical strength etc. Boussemghoune et all [3] worked on the fabrication of a tubular shaped membrane by the slip casting method using zirconium oxide (ZrO2) and kaolin. Characterization of membrane were performed by Scanning Electron Microscopy (SEM), X-ray Fluorescence (XRF), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), and Raman Spectroscopy. The fabricated membrane was tested to treat drinking water obtained from different zones. The experimental parameters such as permeate flux, turbidity were observed. The results showed that the outer surface was much more porous than the inner surface, with filtration time the permeate flux of the raw water decreased, due to a rejection of the organic matters contained in the water. Ma, J., Lu, C., & Zhu, L. (2019) [8] highlighted the key characteristics and advantages of ceramic membranes, such as high chemical and thermal stability, excellent mechanical strength, and resistance to fouling. It also discusses the influence of pore structure, surface properties, and membrane surface modification on the performance and separation efficiency of ceramic membranes.Ashim Kumar Basumatary et all [26] constructed and characterized of MCM-41-ceramic composite membrane by hydrothermal synthesis method. The average pore size of support was found 1 mm and MCM-41-ceramic composite membrane was estimated to be 0.173 mm. It has been observed that at a constant pressure (207 kPa) with varying concentration (250 to 3000ppm) and at a natural pH then the rejection rate of chromium increases as the concentration of the feed increases from 250 to 2000ppm and after 2000ppm there was no effect on concentration. . The optimum rejection rate of 80% is noticed at acidic pH (pH 2) for the feed concentration of 1000 ppm with an applied pressure of 207 kPa. Amin et all [4] worked on the fabrication and characterization of ceramic membrane. These type of ceramic membranes were fabricated by extrusion method from different composition of CuZn on (Clay, TiO2, Carbon and PVA), Porosity and Apparent density were determined by using standard methods for ceramic materials. Erdem et all [7] works on Sol-gel Applications for Ceramic Membrane Preparation using powders (e.g. alumina (A1203), titania (TiO2)) or some clay like ground ceramic powders.Ceramic membranes have a multilayer structure. Ceramic membranes are better choices for pressure driven filtration applications where harsh conditions are present, since they possess superior chemical, thermal, microbiological Solid state method. Tape casting method, Pressing method, Sol-gel method, Extrusion method, Dip coating method, Anodic oxidation method, Chemical vapour deposition (CVD) method. Many successful attempts were performed to use traditional raw materials with modified techniques and to incorporate different types of waste into the production of low-cost ceramic membranes. Smith, A., Johnson, B., Anderson, C. (2017) investigated the effects of sintering temperature and time on the fabrication and performance of kaolin-based ceramic membranes. The results showed that higher sintering temperature and longer sintering time led to increased densification and reduced pore size of the membranes. This resulted in improved filtration efficiency and fouling resistance, making the membranes suitable for wastewater treatment applications. Chen, L., Wang, Y., Li, J. (2018) [7] investigated the performance of kaolin clay-based ceramic membranes for oily wastewater treatment. They modified the membrane surface with hydrophobic materials, which significantly improved the flux and oil rejection rate. The modified membranes exhibited excellent antifouling properties, making them effective for oily wastewater treatment applications.They sintered the membrane at 1150 ° C and obtained the porosity 51% and pore size 4.5 micrometer. Gupta, V., Sharma, S., Yadav, A. (2020) et all developed kaolin clay-based ceramic membranes for industrial wastewater treatment. They optimized the membrane composition and fabrication process to achieve high permeability, excellent chemical resistance, and stable performance. The membranes effectively removed various pollutants, including heavy metals and organic contaminants, from industrial wastewater, making them suitable for industrial effluent treatment. Wang, Q., Liu, L., Zhang, J. (2020) fabricated and charactersed the kaolin-based ceramic membranes for the removal of heavy metal ions from wastewater. The results demonstrated that the membranes had high adsorption capacity and selectivity for heavy metal ions due to the surface properties and pore structure. The membranes exhibited excellent removal efficiency for heavy metal ions, making them effective for wastewater treatment applications.They were able to remove 85% heavy metal and porosity was 65%. Zhang, H., Zhou, Y., Xu, M. (2020) investigated the antifouling performance of kaolin clay-based ceramic membranes for oily wastewater treatment. They modified the membrane surface with hydrophilic coatings, which improved the membrane's resistance to fouling by oil droplets. The modified membranes showed enhanced flux recovery and prolonged operation time, indicating their potential for long-term and efficient oily wastewater treatment. Li, H., Wang, X., Liu, J. (2021) characterized kaolin-based ceramic membranes for pharmaceutical wastewater treatment. The membranes exhibited excellent removal efficiency for pharmaceutical compounds, such as antibiotics and hormones, due to their pore size of 1.2 micrometer and surface properties. The membranes also demonstrated good stability and resistance to chemical degradation(less than 3 %), making them suitable for treating pharmaceutical wastewater. Yang, J., Wu, Y., Zhang, Y. (2021) investigated the effect of surface modification on the performance of kaolin clay-based ceramic membranes for dye removal. They modified the membrane surface with functional groups, which improved the membrane's adsorption capacity and selectivity for dyes. The modified membranes exhibited high dye removal efficiency and good regeneration potential, indicating their potential for dye wastewater treatment.

CHAPTER 3

MEMBRANE PREPARATION

Selection of raw materials is the crucial part for producing any desired membrane with the targeted characteristics. We have choose the raw materials as per the objective of waste water treatment ,strength and cheap in cost.

3.1.SELECTION OF RAW MATERIALS

The proportions of the raw materials used to make a ceramic membrane will depend on the specific requirements of the membrane and the desired properties of the finished product. Some factors that may influence the proportion of raw materials used include:

1. **Type of ceramic material**: The type of ceramic material being used will determine the overall composition of the membrane. Different ceramic materials will have different properties and will require different proportions of raw materials to achieve the desired result.

2. **Porosity**: The porosity of the ceramic membrane can be controlled by adjusting the proportion of binders and pore-forming agents used in the mixture. A higher proportion of binder will result in a more dense, less porous membrane, while a higher proportion of pore-forming agents will result in a more porous membrane.

3. **Strength**: The strength of the ceramic membrane can be affected by the proportion of binders and reinforcing agents used in the mixture. A higher proportion of binder will result in a stronger, more rigid membrane, while a higher proportion of reinforcing agents will increase the tensile strength of the membrane.

4. **Chemical resistance**: The chemical resistance of the ceramic membrane can be influenced by the proportion of corrosion-resistant materials used in the mixture. For example, using a higher proportion of corrosion-resistant ceramics or coatings can improve the chemical resistance of the membrane.

3.2 PROPERTIES OF RAW MATERIALS

3.2.1 Kaolin ($Al_2O_3 . 2SiO_2 . 2H_2O$)

Kaolin is a soft, white, clay-like material composed mainly of the mineral kaolin, which is a hydrated aluminum silicate. It has several properties, including:

- **Refined and porous:** Kaolin has a fine, powdery texture and is highly porous, which makes it ideal for use in ceramics, paper, and other applications where a smooth, refined surface is desired.
- **Insoluble in water:** Kaolin is insoluble in water, which makes it useful for applications where it needs to remain stable in a wet environment.
- **Non-abrasive:** Kaolin is a soft, non-abrasive material that is gentle on the skin and does not scratch or damage surfaces.
- **Odorless:** Kaolin is an odorless material, which makes it suitable for use in applications where a strong smell would be undesirable.
- **Non-toxic:** Kaolin is generally considered to be non-toxic and is safe for use in a variety of applications, including food processing and cosmetics.
- **High melting point:** Kaolin has a high melting point, which makes it useful in applications where it needs to withstand high temperatures.
- **Chemically resistant:** Kaolin is resistant to most acids and alkalis, which makes it useful in a variety of industrial applications.
- **Good insulator:** Kaolin has good insulating properties, which makes it useful in the manufacture of electrical cables and other insulation materials.

Kaolin is used as base material as it has higher refractory properties and low plasticity. At the same , it is inert in nature and doesn't contaminate during treatment.

3.2.2 Feldspar

Feldspar is a group of minerals that belongs to the tectosilicate family. It is one of the most abundant minerals found in the Earth's crust, comprising approximately 60% of it. Feldspar is primarily composed of aluminum silicates, along with varying proportions of potassium, sodium, and calcium ions.

Properties of feldspar include

- **Hardness**: It is typically ranging from 6 to 6.5 on the Mohs scale.
- **Physical Behaviour** :It has a glassy or pearly luster and can occur in various colors, such as white, pink, gray, or brown. Feldspar exhibits a characteristic cleavage, forming two planes that intersect at nearly a right angle.
- **Melting point**: It has a relatively low melting point, allowing it to melt and fuse with other minerals during the sintering process.

In ceramic membrane fabrication, feldspar plays a crucial role as a fluxing agent. It helps to lower the melting point of the ceramic mixture, allowing for sintering and densification at lower temperatures. By promoting the fusion of other ceramic materials, feldspar enhances the mechanical strength and stability of the resulting ceramic membranes.

3.2.3 Carboxy Methyl Cellulose (CMC)

Sodium carboxymethylcellulose (CMC) is a water-soluble polymer that is often used as a binder in the manufacture of ceramic membranes. It is a derivative of cellulose, which is the main structural component of plant cell walls. Sodium carboxymethyl cellulose (CMC or NaCMC) is a water-soluble, white, odorless, tasteless polymer derived from cellulose. It has a number of properties, including:

- **Water solubility**: CMC is highly water-soluble and forms a clear, viscous solution when dissolved in water. The solubility of CMC depends on the degree of substitution (the degree to which the cellulose molecules are modified), the pH of the water, and the temperature.
- **Viscosity**: CMC has the ability to increase the viscosity of water and other solutions, making it useful as a thickening agent. The viscosity of a CMC solution can be adjusted by changing the concentration of CMC, the pH, and the temperature.
- **Stability**: CMC solutions are stable over a wide pH range and are resistant to bacterial and enzymatic degradation.
- **Film-forming ability**: CMC can form clear, flexible films when it is dissolved in water and then dried. These films are resistant to oil, grease, and many chemicals.
- **Adhesiveness**: CMC has good adhesive properties and can be used as a bonding agent in a variety of applications.
- **Non-toxic**: CMC is generally considered non-toxic and is safe for use in food, pharmaceutical, and personal care products.
- **Biodegradability**: CMC is biodegradable, which means it can be broken down by micro-organisms into its component parts. This makes it an attractive material for

3.2.4 Quartz

Quartz is a type of mineral that is often used in the manufacture of ceramic membranes. It is a naturally occurring silicate mineral that is composed mainly of silicon dioxide (SiO2). Quartz is known for its high chemical stability, low coefficient of thermal expansion, and excellent thermal and mechanical properties. Some specific properties of quartz include:

- **High melting point**: Quartz has a high melting point of about 1713 °C, which makes it resistant to high temperatures.
- **Low coefficient of thermal expansion**: Quartz has a low coefficient of thermal expansion, which means that it does not expand or contract significantly when exposed to changes in temperature. This makes it suitable for use in applications where dimensional stability is important.
- **Excellent thermal conductivity**: Quartz has good thermal conductivity, which means that it is able to transfer heat effectively. This makes it useful in applications where heat transfer is important.
- **Good chemical stability**: Quartz is resistant to attack by most acids, bases, and organic solvents. It is also resistant to corrosion and does not react with other materials under normal conditions.
- **High hardness**: Quartz is a hard, abrasive material with a Mohs hardness of 7. This makes it resistant to wear and abrasion, which makes it useful in applications where durability is important.
- **High mechanical strength**: Quartz has high tensile and compressive strength, which makes it resistant to breaking and deformation under stress. It is also brittle, which means that it is prone to cracking or breaking when subjected to impact or shock.

Quartz is used in producing ceramic membrane due to its shinning properties and mechanical strength which it induces in it.

3.2.5 Calcium Carbonate ($CaCO_3$)

Calcium carbonate is a chemical compound with the formula $CaCO3$. It is a common substance found in rocks as the minerals calcite and aragonite (most notably as limestone, which is a type of sedimentary rock consisting mainly of calcite).

- **Chemical Composition**: Calcium carbonate is composed of calcium (Ca), carbon (C), and oxygen (O) atoms in a 1:1:3 ratio.
- **Appearance**: Calcium carbonate occurs naturally in the form of white, odorless powder or colorless crystals.
- **Solubility**: It is sparingly soluble in water, but readily dissolves in acids, such as hydrochloric acid, to form calcium chloride and carbon dioxide gas.
- **Density**: The density of calcium carbonate varies depending on its crystalline structure and form. Typically, it has a density ranging from 2.7 to 2.9 g/cm3.
- **Hardness**: Calcium carbonate exhibits a relatively low hardness of around 3 on the Mohs scale, making it susceptible to scratching.

These properties make calcium carbonate a versatile and important compound used in various industries and applications.Here we are using Calcium Carbonate to add pores in the Ceramic Membrane. When Calcium Carbonate is heated it decompose to form Calcium Oxide and Carbon Dioxide. Here Carbon Dioxide moves out from the membrane creating pores.

3.2.6 Boric acid (H_3BO_3)

Boric acid, more specifically orthoboric acid, is a compound of boron, oxygen, and hydrogen with formula B(OH)3. It may also be called hydrogen borate or boracic acid. It is usually encountered as colorless crystals or a white powder,

- **Chemical Composition**: Boric acid is composed of boron (B), hydrogen (H), and oxygen (O) atoms in a 1:3:3 ratio.
- **Appearance**: It is a white, crystalline solid that can be in the form of powder or granules.
- **Solubility**: Boric acid is soluble in water and forms a weakly acidic solution. The solubility increases with higher temperatures.
- **Melting Point**: The melting point of boric acid is relatively low, around 170-180°C.
- **Borate Salts**: Boric acid can form borate salts when reacting with bases or metal oxides. These salts find applications in various industries, including glass manufacturing, ceramics, and detergent production.

Here in our Ceramic Membrane we are using Boric Acid for strength and to improve the thermal properties of the Membrane.

3.3 COMPOSITION OF RAW MATERIALS

Compositions are found on a basis of 450 gm (Dry Basis)

Si No	**Name**	**Percentage**	**Amount**
1	Kaolin	37%	166.5gm
2	Feldspar	7%	31.5 gm
3	Calcium Carbonate	26%	117 gm
4	Boric Acid	8%	36 gm
5	Carboxymethyl Cellulose	4%	18 gm
6	Quartz	20%	90gm

Table 3.1 : Composition of Raw Materials

3.4 PREPARATION OF MEMBRANE

There are several steps involved in the process of making a ceramic membrane. They are explained below:

- **Raw material preparation**: The first step in the process is to prepare the raw materials that will be used to make the ceramic membrane. Here raw materials are Kaolin , Calcium Carbonate , Boric Acid , Carboxymethyl Cellulose , Feldspar and Quartz. Here all the raw materials are passed through sieve to get homogeneous size distribution and avoid lumps. Then raw materials are mixed together to create a homogeneous mixer.
- **Mould Preparation**: Here the binding agents Carboxymethyl Cellulose mixed with all the other materials in the tray, to make dough which is suitable to mould in our required shape .

Fig 3.1: Prepared Dough

- **Tube extrusion**: The next step is to extrude the dough through a tube-shaped die to create the desired shape of the ceramic membrane. This can be done using a variety of extrusion techniques, such as pressure extrusion or centrifugal extrusion.The dough is fed into the extruder resulting tubular shaped membranes with the help of a die Attaining 150–200 mm length the tubular shaped membranes are cut with the help of a sharp blade.

Fig 3.2: Extrusion

- **Natural Drying**: After extrusion, the ceramic membrane must be dried to remove any excess water. This can be done using a variety of methods, including air drying, oven drying, or freeze drying. Depending upon the atmospheric condition it is dried for at least 24 hrs.

Fig 3..3: Natural drying of Membranes

- **Sintering** : Once the ceramic membrane is dry, it must be sintered, or fired, to consolidate the particles and create a solid, porous structure. For this purpose the raw membranes are sintered in the stepwise mufflfle furnace at different temperatures at the heating rate of 0.5 C per min. The fabricated membrane are heated to 100 C for 24 hrs, 200 C for 24 hrs and finally sintered for 6 hrs at 950°C.

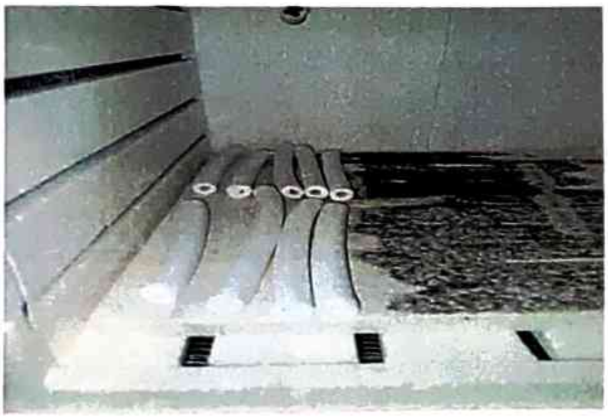

Fig 3.4:Membranes kept in Muffle Furnace

Fig 3.5: Muffle Furnace

- **Finishing** : After sintering, the ceramic membrane may undergo additional finishing processes, such as glazing or coating, to improve its performance or aesthetic properties.

- **Testing**: Before the ceramic membrane is ready for use, it must be tested to ensure that it meets the required specifications. This may involve evaluating its physical and chemical properties, as well as its performance under different conditions.

- **Assembly**: Finally, the individual tubular ceramic membranes are typically assembled into a larger system, such as a module or a stack, for use in filtration or separation applications.

3.5 CHARACTERISATION TEECHNIQUE

Characterization of the synthesized membrane includes porosity of the membrane which is measured using Millipore water for soaking. For chemical stability and durability. acid and base test is performed. For this test, 2 pH sulphuric acid and 12 pH sodium hydroxide is selected. This test basically measures the loss of mass due to corrosion after keeping the fabricated membrane in strong and rough environment. The water permeability test was carried out using milipore water to find the pure water flux through the membrane.Porosity: The porosity of a ceramic membrane can be determined by measuring the amount of gas or liquid that is able to pass through the membrane.Detail procedure is given below:

3.5.1 Porosity:

To fulfil the objective of separation, porosity of the membrane must be determined.. Porosity is defined as the ratio of volume of pores to the volume of the membrane. Here the porosity is measured using Millipore water for soaking the membrane over a span of one week.

Fig 3.6: Sonicator

1) One small piece of nicely cut and smoothened membrane is kept in a beaker, the beaker is then filled with millipore water.

2) The beaker is kept in the sonicator for 15 minutes for sonification in order to separate loose particles adhered to the membrane which is caused due to the vibrations produced in the millipore water through electrosonic waves.

3) After the process is done the membrane is pet dry in napkin paper and then the membrane is heated in hot air oven at 120° C for 4 hours.

4) Then we take dry weight W_1.

5) Now we soak the membrane in Millipore water 1 week. Then we take the weight as a wet weight, W_2.

3.5.2 Chemical Stability

The chemical resistance of the membrane is tested by subjecting the membrane to acidic and basic solution. For this pH 2 solution of H_2SO_4 and pH 12 solution of NaOH is used. The membranes are kept in the solution for a week at ambient temperature. Further, the ceramic membrane was evaluated for net weight loss due to exposure to corrosive environment.

Fig 3.7 : Measuring the weight

Process Description:

1) One small piece of nicely cut and smoothened membrane is kept in a beaker, the beaker is then filled with millipore water.

2) The beaker is kept in the sonicator for 15 minutes for sonification in order to separate loose particles adhered to the membrane which is caused due to the vibrations produced in the millipore water through electro sonic waves.

3) After the process is done the membrane is pet dry in napkin paper and then the membrane is heated in hot air oven at 120°C for 4 hours.

4) Then we take dry weight W_1.

5)We prepared 2nd solutions i.c. acidic solution of 2 pH using sulphuric acid and base solution using sodium hydroxide of 12 pH.

6) Then we kept the two dry membrane pieces in each of the solutions and both the solutions along with the membranes was kept undisturbed for 1 week

7) After 1 week we took out the membranes and dried them in a hot air oven for 3-4 hours at 110° C. Then the change of weight is measured .

3.5.3 Water Flux test

The water flux test was carried out to find the pure water flux using Millipore water which is then used to find the pore size of the membrane using the Hagen-Poiseullie equation. It was carried out at a range of pressure from 13.8-68.95 kPa at a fixed volumetric flow rate of 20 LPH. The permeate was collected for an interval of 2 mins between each consecutive pressure.

Process Description:

1) We take the prepared membrane and cut it (9.1 cm) and file it to fit inside the apparatus tube.
2) In a bucket we take about 3 L of milipore water and turn on the machine at a low speed in a constant flow rate.

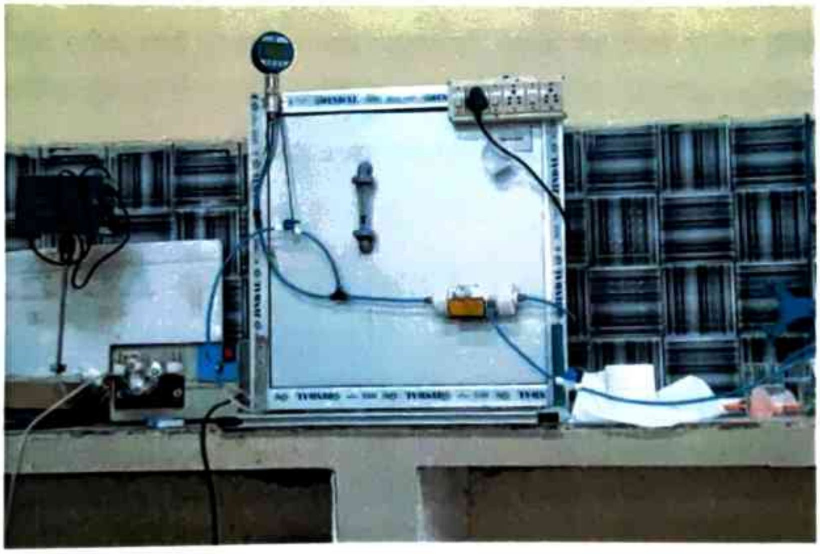

Fig 3.8: Crossflow set up For Water Flux Test

3) Milipore water is allowed to pass through the membrane at high pressure to remove any loose particle in the membrane for about an hour.

4) The pure water flux is then measured by measuring the volume of permeate collected at different pressures ranging from 13.8 to 68.95 kPa for the time interval of 2 mins.

5) The experiment is run again to get two sets of reading for an average value.

Cross Flow set up for water flux test-

The equipment comprises of a series of feed tank, a tubular shaped membrane module, a peristaltic pump for circulation of the feed solution, a pressure indicator and a flow meter to measure the cross flow rate along with 3 control valves. The tubular shaped ceramic membrane was fitted into the module. The membrane module comprises of one hollow and two bolt parts that were made up of plastic. The membrane was fixed between the two bolt parts and the two ends were joined. Each end consists of a pipe and at the middle there was another pipe i.e. the feed pumps from the feed tank to the module through one pipe at one end and at the other end retentate was received, again the pipe at the middle of the module gives the permeate which was flowing through the membrane. The pressure was adjusted by using those 3 control valves which were located at the flowpaths.

3.5.4 COD Determination:

Experimental Procedure for Determining COD of Waste Water Sample

- **Equipment and Chemicals:**

COD reactor, Waste water sample, Potassium dichromate ($K_2Cr_2O_7$) solution (0.25 N), Silver sulfate (Ag_2SO_4) catalyst ,Sulfuric acid (H_2SO_4) solution (1.0 N), Distilled water, digestion tubes, Burette, Hot plate, Spectrophotometer, Pipettes, burettes, and other standard laboratory equipment

- **Process Description**:

1) We take 10 ml of sample and add 40 ml of distil water in a test tube.
2) We make a control sample using 50 ml of distil water.
3) A pinch of Silver Sulfate is added to the samples.

Fig 3.9: COD Digestor

4) 10 ml of N/10 K2Cr2O7 (Potassium Dichromate) is added to all the samples.

5) 50 ml of concentrated Sulfuric acid (98%) is added to the samples.

6) Then we place all the samples in the COD digester and heat them for 1 hour at 150°C.

7) Then the samples are cooled to room temperature in a water bath for about 20 minutes.

8) The samples are then titrated against 0.IN Ferrous Ammonium Sulfate adding 5-6 drops of Ferroin indicator in the sample and the readings are noted.

All the experiments were carried out at ambient temperature at different applied pressure in the range of 1 to 5 psi at a constant volumetric flow rate of 20 LPH at an interval of 5 minutes. All the experiments were conducted twice and the average values are reported. The percentage of COD Removal is calculated from the expression

COD=((C-sample reading)x8x1000x f)/ Volume of sample
COD removal = $(1-C_p/C_f) * 100$;
Where, C, is the COD of the permeate

C_f is the COD of the raw feed

3.5.5 BOD Determination:

Experimental Procedure for Determining BOD_5 of Waste water Sample

1. **Equipment and Chemicals**:

BOD bottles (300 mL capacity), Dilution water (dechlorinated tap water), Wastewater sample, Incubator, BOD incubation rack, pH meter, Dissolved oxygen (DO) meter, Sodium thiosulfate solution (0.025 N), Manganese sulfate solution (MnSO4-H2O) (8 g/L), Alkaline potassium iodide solution (KOH-I2) (50 g/L), Sulfuric acid (H2SO4) (1 N), Pipettes, burettes, and other standard laboratory equipment.

2. **Sample Dilution**:

A series of dilutions were prepared by adding appropriate volumes of the wastewater sample to BOD bottles filled with the dechlorinated tap water. The dilutions were carefully calculated to ensure that the BOD_5 fell within the acceptable range of 20-300 mg/L. A 1:10 dilution ratio was chosen as a starting point.

Fig 3.10: BOD Incubator

3. **Chemical Additions:**

To each BOD bottle, 2 mL of alkaline potassium iodide solution ($KOH-I_2$) and 2 mL of manganese sulfate solution ($MnSO_4.H_2O$) were added. These chemical additions facilitated the reaction between dissolved oxygen and organic matter during the incubation period.

4. **Initial DO Measurement** :

The DO content of each BOD bottle was measured using 2 ml H2SO4 , Starch Solution titrating against 0.025N Sodium Thiosulphate solution immediately after the chemical additions. These initial DO values were recorded for further analysis.

5. **Incubation:**

All the BOD bottles, including the seed control, were placed in a dark incubator at a constant temperature of 20°C ± 1°C. The bottles were incubated undisturbed for a period of 5 days (120 hours) to allow for microbial decomposition of the organic matter present in the wastewater sample.

6. **Final DO Measurement :**

After the 5-day incubation period, each BOD bottle was removed from the incubator, and the DO content was measured. The final DO values were recorded for subsequent calculations.

7. **Blank Control:**

A blank control BOD bottle containing the millipore water and the chemical additions was prepared. This blank control accounted for any DO changes unrelated to biological activity, helping to ensure accurate BOD measurements.

8. Titrations:

The blank control bottle and the seed control bottle were individually titrated using sodium thiosulfate solution (0.025 N) until a pale yellow color persisted. The volume of thiosulfate solution used in each titration was noted for further calculations.

9. BOD Calculation:

The BOD5 of the wastewater sample was calculated using the following formula:
BOD5 (mg/L) = [(DO initial - DO final) × (thiosulfate volume)] / [(sample volume) × (seed control volume)]

In this formula, the DO initial and DO final represent the initial and final DO values, respectively. The thiosulfate volume is the volume of sodium thiosulfate solution used in the titration of the blank control and seed control bottles. The sample volume refers to the volume of the wastewater sample used, and the seed control volume is the volume of the seed control bottle. By substituting these values, the BOD5 of the wastewater sample can be calculated.

CHAPTER 4

RESULT AND DISCUSSION

4.1. Porosity

The Calculations were performed as follows:-

Dry weight of the membrane is taken as W_1

Weight of the membrane after one week is taken as W_2

Difference between initial and final weight is $W_3=W_2-W_1$

Table 4:1: Porosity Determination Test

TRIAL	W_1(g)	W_2(g)	Porosity,φ $(W_2-W_1)/W_1$	% Porosity
Trial 1	7.0879	9.689	0.33703	33.703
Trial 2	7.090	9.204	0.304	30.4
Average Porosity				32.015

The Average Porosity is determined as : 32.015 %

4.2. Chemical Stability Test

The Calculations are given below:

Lets say the dry weight of the membrane is W_1(g)

The weight after one week is W_2(g)

Difference between initial and final weight is $W_3=W_2-W_1$

Table 4.2. Acid Test Observation

TRIAL	W_1(g)	W_2(g)	W_3(g)	Fractional weight loss of the sample	% Weight loss
Trial 1	3.219	3.152	0.067	0.0208	2.08
Trial 2	3.569	3.496	0.073	0.027	2.27
Mean % Loss					2.175

The mean percentage loss of weight in acid test is : 2.175 %

Table 4.3: Base Test Observation

TRIAL	W_1(g)	W_2(g)	W_3(g)	Fractional weight loss of the sample	% Weight loss
Trial 1	2.263	2.21	0.053	0.0234	2.34
Trial 2	2.27	2.221	0.049	0.02209	2.209
Mean % Loss					2.274

The mean percentage loss of weight in base test is : 2.274 %

4.3 Water Flux Test

Table 4.4 : Pressure vs Volume data Set 1

Permeate(1psi) x10^{-5}	Time(sec)	Permeate(2psi)	Permeate(3psi)	Permeate(4psi)	Permeate (5psi)
230	300	284	326	390	430
228	600	280	324	384	426
226	900	282	322	384	424
224	1200	276	320	382	420
222	1500	272	320	380	416
220	1800	275	318	376	412
216	2100	276	318	372	410
212	2400	274	316	370	406
212	2700	272	312	370	404
212	3000	270	314	368	402
212	3300	270	310	368	400
212	3600	270	306	368	404

Table 4.5: Pressure vs Volume data set 2

Permeate(1psi) x10^{-5}	Time(sec)	Permeate(2psi)x10^{-5}	Permeate(3psi)x10^{-5}	Permeate(4psi)x10^{-5}	Permeate (5psi)x10^{-5}
232	300	288	330	390	440
228	600	280	324	384	432
226	900	282	324	384	430
224	1200	276	320	382	428
224	1500	274	322	380	424
220	1800	275	316	376	426
216	2100	276	312	372	420
210	2400	272	310	370	412
210	2700	272	306	370	410
212	3000	268	308	368	408
210	3300	266	306	368	406
206	3600	260	306	368	404

Table 4.6 Pressure vs Permeate(avg) vs Least Square fitting Correction of Water Flux data set 1

Pressure(psi)	Permeate x10^{-5}(avg)	Least Square Fitting of Permeate
1	218.24	216.922
2	271.66	268.272
3	313.33	319.624
4	368.33	370.97
5	420	422.326

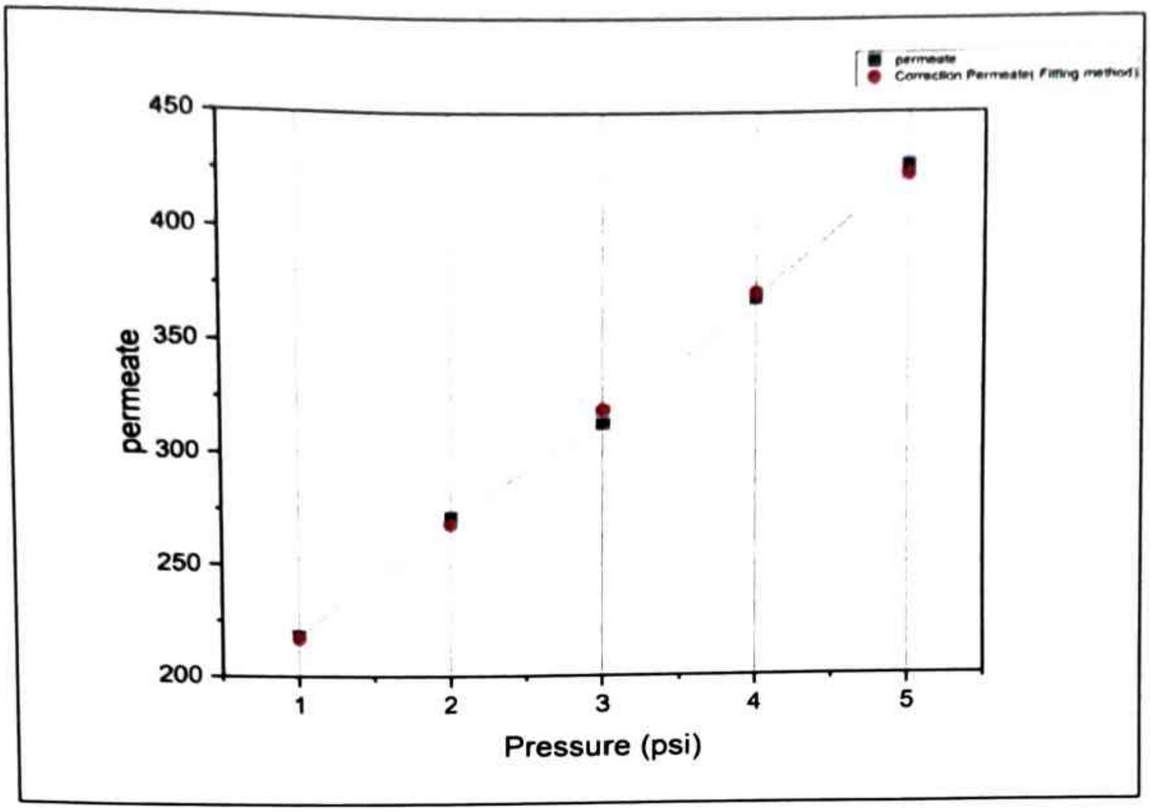

Fig 4.1: Pure Water Flux as function of applied pressure for data set 1

Table 4.7 Pressure vs Permeate(avg) vs Least Square fitting Correction of Water Flux data set 2

Pressure(psi)	Permeate x10^{-5}(avg)	Least Square Fitting of Permeate
1	218.1666667	218.274
2	274.0833333	268
3	315.3333333	318.32
4	368.33	368.331
5	426.66	418.35

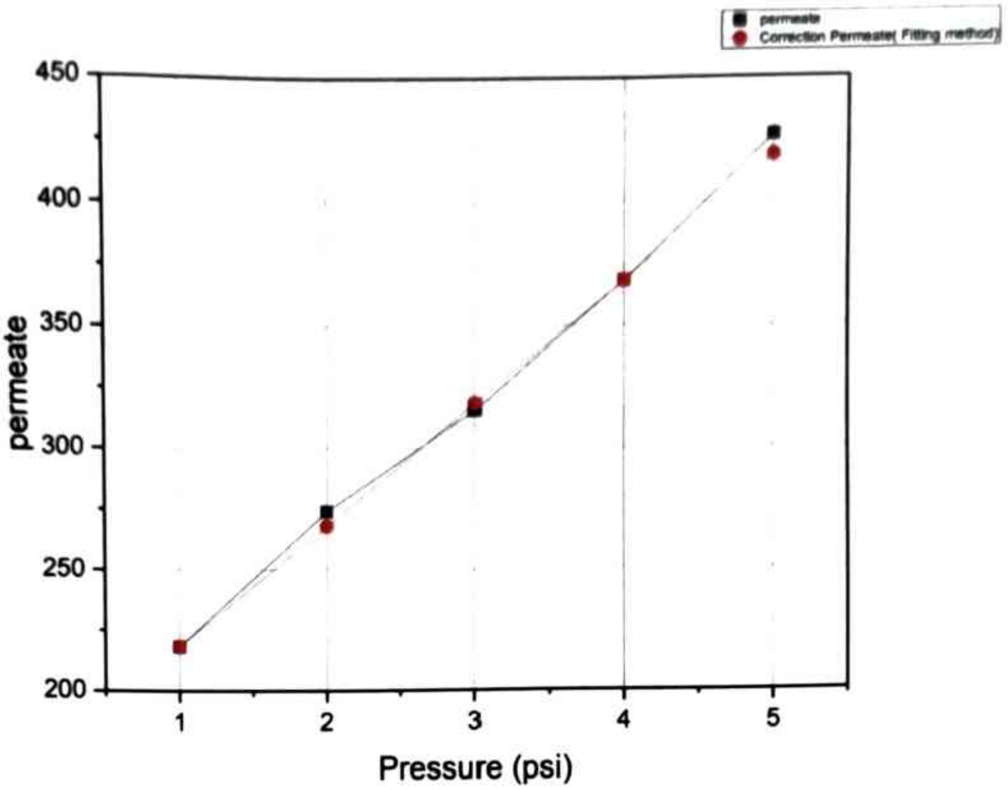

Fig 4.2: Pure water flux as a function of applied pressure for

Slope obtained from the graph is 7.25×10^{-8}.(on average)

The Water Permeability L_h is now calculated from the slope of pure water flux by using the Darcy's Equation

$Jw = L_h \times \Delta P$

Thus, $L_h = 3.4 \times 10^{-8}$ m/s.Pa

Now using the Hagen-Poiseuille's Equation, considering cylinderical pores,

$Jw=\varepsilon . R^2 \Delta P/8\mu\tau$

Using the above equation with porosity=0.32015 and viscosity of water as 0.00089 Pas. , τ is assumed to be 1, and pore length is 0.0006m . Placing the values and combining the equations, we get the value of $R= 6.6x10^{-5}$ m or diameter is equal to 1.2 μm.

Thus the pore size is determined as 1.2 μm.

Since the pore size ranges between 0.1-3μm, so the membrane faciltates micro filtration.

4.3.1 Pressure vs Permeate Flux data for waste water

Table 4.8: Pressure vs Permeate flux data of Airport Waste water

Permeate(1psi) $x10^{-5}$	Time(min)	Permeate(2psi)	Permeate (3 psi)	Permeate (4 psi)	Permeate (5 psi)
247.49	10	330	410	480	560
230	20	300	350	430	500
212	30	270	300	380	430
210	40	260	290	340	400
210	50	240	270	300	350
200	60	230	260	280	320

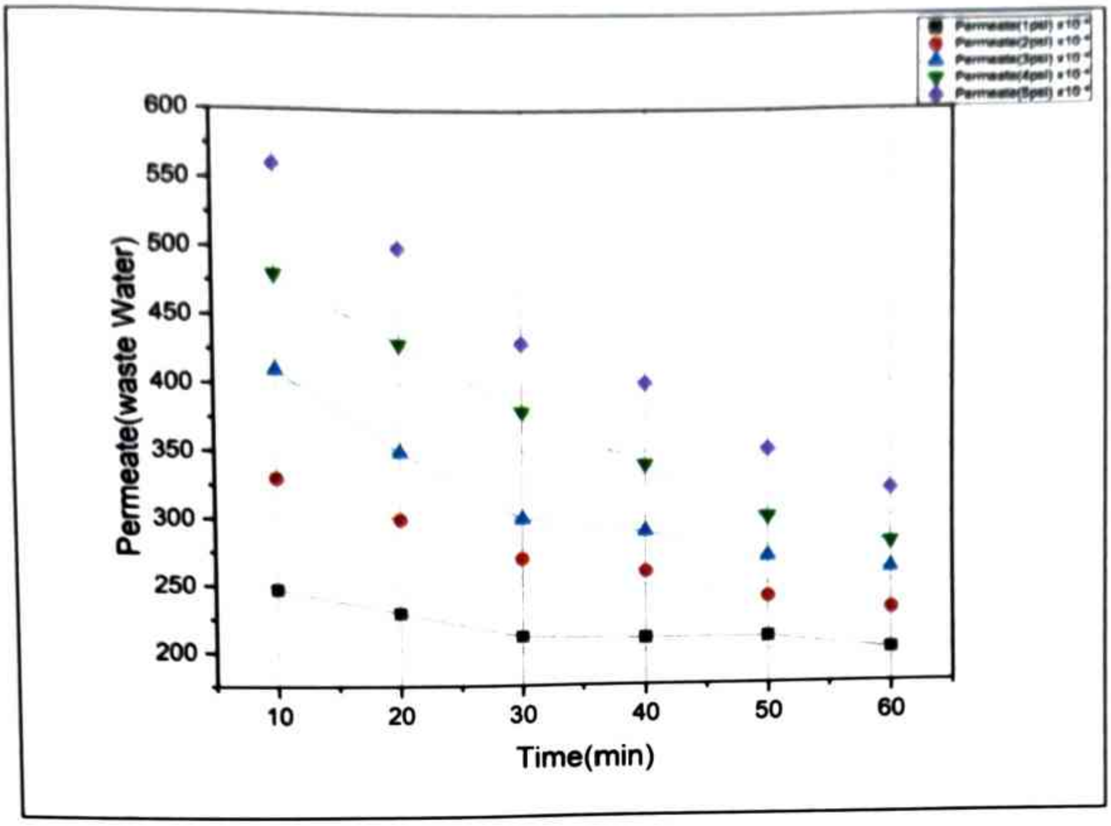

Fig 4.3: Waste Water graph for time vs permeate with variation of pressure

It can be seen clearly that the permeate flux decreases over time during the microfiltration. This decrease is due to concentration polarization on the membrane surface and blocking of the pores of the membrane. Thus the flux decreases and hence the permeation through the membrane decreases. However it has been seen that with the increase in pressure, the permeate flux increases. The permeate flux profile is however not linear. This is likely due to concentration polarization and adsorption of suspended particles of waste water on the pores, which thus creates resistance to the flow.

4.4. COD determination of Waste Water

Pressure	Time	COD Removal %	COD Values(mg/L)	Sample No.	Average COD Removal %
1	10	33.14	304	1	32.23214286
	20	32.58	302	2	
	30	32.60	306	3	
	40	32.03	300	4	
	50	32.34	304	5	
	60	31.69	306	6	
2	10	29.67	324	1	28.125
	20	29.14	320	2	
	30	29.12	322	3	
	40	28.67	324	4	
	50	29.12	322	5	
	60	27.57	320	6	
3	10	26.33	336	1	24.25595238
	20	25.89	338	2	
	30	25.78	342	3	
	40	24.83	340	4	
	50	25.24	338	5	
	60	24.89	342	6	
4	10	25.00	330	1	26.11607143
	20	24.55	332	2	
	30	24.66	328	3	
	40	24.10	330	4	
	50	24.45	334	5	
	60	23.86	332	6	

5	10	24.02	342	1	23.17708333
	20	23.36	344	2	
	30	23.40	346	3	
	40	23.11	342	4	
	50	23.49	345	5	
	60	22.76	346	6	
COD value of raw feed: 448 mg/L					

Table 4.9: COD removal at different pressures of waste water

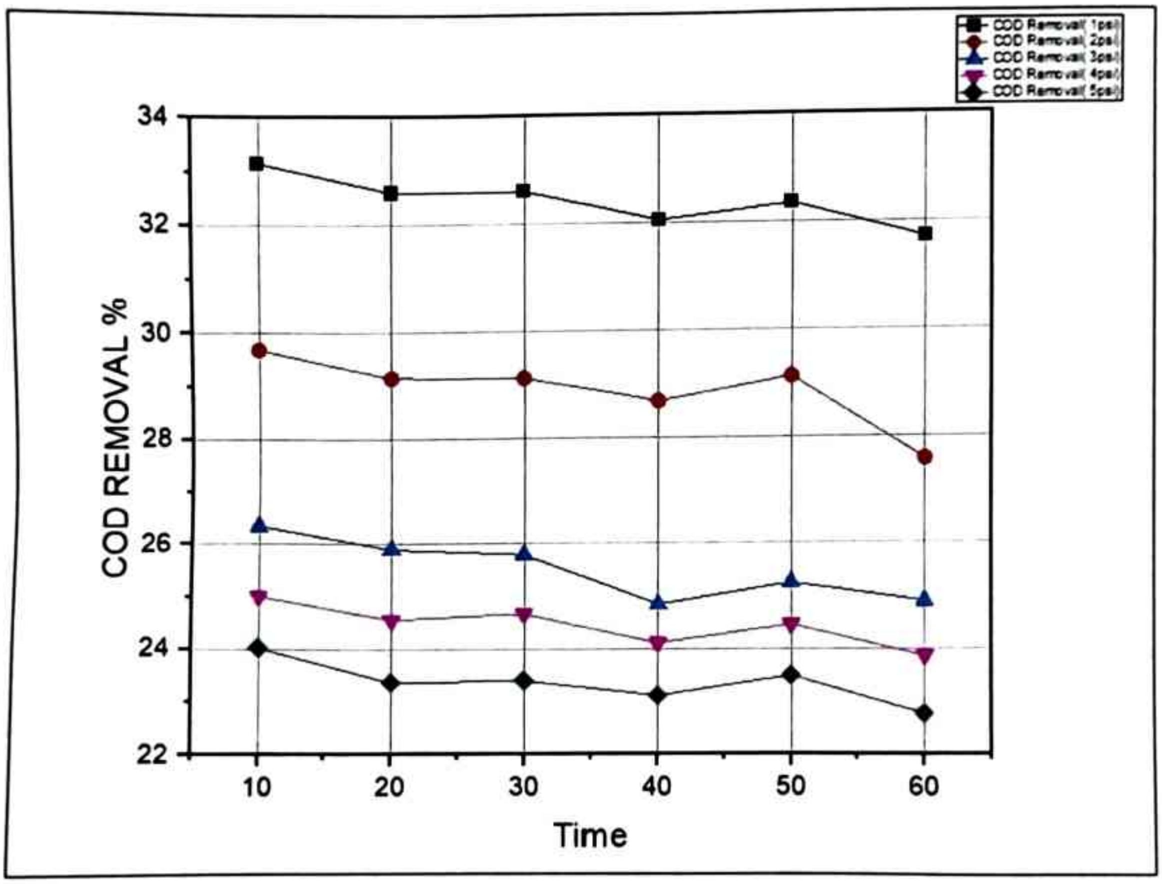

Fig. 4.5: COD Removal as a Function of Time

4.5: BOD Removal Percentage from Waste water

Table 4.10: BOD removal at different pressures of waste water

Pressure	Time(min)	BOD Removal %	BOD Values(mg/L)	Sample	Average BOD Removal %
1	10	44.38	196	1	44.38202247
	20	43.25	198	2	
	30	44.38	202	3	
	40	43.44	198	4	
	50	42.24	196	5	
	60	44.38	198	6	
2	10	37.07	225	1	37.03183521
	20	37.92	224	2	
	30	36.79	221	3	
	40	36.81	225	4	
	50	36.07	226	5	
	60	37.07	224	6	
3	10	34.26	232	1	34.5505618
	20	35.39	234	2	
	30	33.70	230	3	
	40	34.83	236	4	
	50	33.66	232	5	
	60	34.26	234	6	

4	10	31.33	240	1	31.03932584
	20	31.66	248	2	
	30	30.89	244	3	
	40	31.67	246	4	
	50	30.67	250	5	
	60	31.33	245	6	
5	10	29.21	248	1	29.11985019
	20	29.77	252	2	
	30	29.08	250	3	
	40	29.61	256	4	
	50	28.68	252	5	
	60	29.21	256	6	
Original BOD of waste water:					356

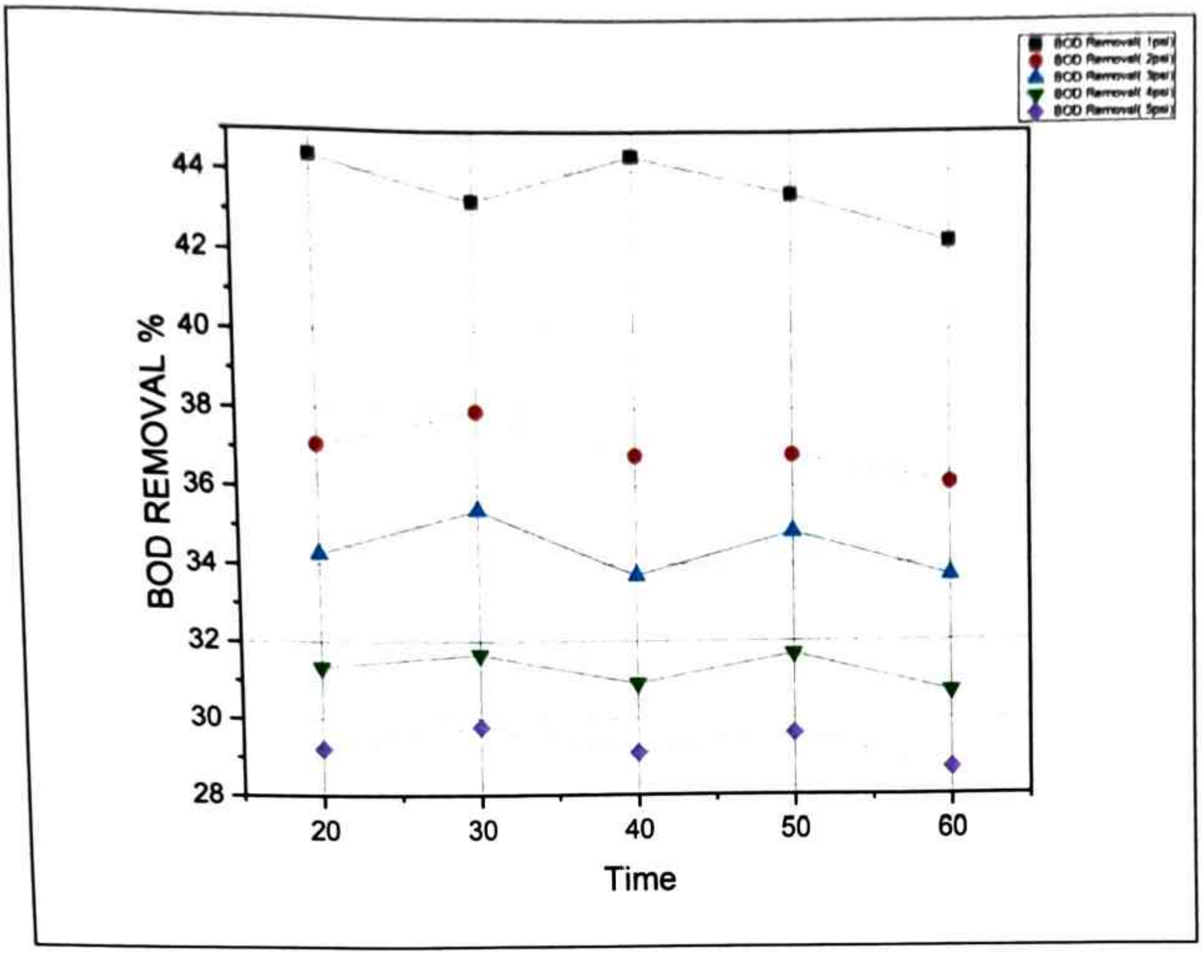

Fig. 4.6: BOD Removal as a Function of Time

The fig. 4.5 shows the removal %of COD from waste water with respect to time for varied pressure applied and the fig 5.6 shows the removal %of BOD from waste water with respect to time for varied pressure applied . It has been found that, at pressure 1 psi, highest percentage of separation is seen. However as the pressure is increased, both the COD and BOD content increases in the permeate stream due to greater driving force through the membrane. At the same, the formation of cake layer over the membrane surface also contributes in COD and BOD removal when the filtration is run for a longer duration of time.

The fabricated membrane hence delivers a peak COD removal of 32.2321% and 44.32% BOD removal at 1 psi pressure.

CHAPTER 5

CONCLUSION

The successful design of a tubular ceramic membrane specifically tailored for the treatment of wastewater was accomplished. In this study, the influence of different applied pressures on both permeate flux and removal of Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) in the wastewater was thoroughly investigated.

The sintering process, a critical stage in membrane fabrication, necessitated the use of an appropriate heating rate. To ensure optimal results, a low heating rate of 0.5° C/min was meticulously employed. The outcomes of the fabrication process revealed a porosity percentage of 32.761% and an average pore size of 1.21 μm, indicating that the prepared membrane falls within the microfiltration range.Subsequently, the fabricated membrane was utilized to treat wastewater obtained from Airport Authority of India at varying pressures. The findings demonstrated that COD and BOD removal increased as the applied pressure on the membrane increased, within the duration of microfiltration. Remarkably, the removal rate exhibited satisfactory performance for the waste water from Airport Authority of India, with a maximum removal efficiency of 32.23% COD and BOD 44.38% achieved at 1 psi under a fixed volumetric flow rate of 10 LPH.Consequently, the prepared microporous membrane exhibited efficient treatment capabilities for wastewater. The successful application of the tubular ceramic membrane in the treatment process highlights its potential as a viable solution for addressing the wastewater treatment .

CHAPTER 6

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PRODUCTION OF FORMALDEHYDE

8th SEMESTER B. TECH PROJECT

Submitted in partial fulfillment of
the requirements for the Degree of
BACHELOR OF TECHNOLOGY
In
CHEMICAL ENGINEERING
OF
ASSAM SCIENCE AND TECHNOLOGY UNIVERSITY

SUBMITTED BY

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UTPAL BASUMATARY (19/281)
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ANIKET DAS (19/286)

DEPARTMENT OF CHEMICAL ENGINEERING
ASSAM ENGINEERING COLLEGE GUWAHATI-781013
JUNE 2023

CERTIFICATE FROM DEPARTMENT OF CHEMICAL ENGINEERING

This is to certify that project entitled "PRODUCTION OF FORMALDEHYDE" submitted by the following students of 8th semester of Chemical Engineering Department.

1. Chatrapati KamalNarayan Hazarika, 19/279
2. Utpal Basumatary, 19/281
3. Khanita Tayeng, 19/282
4. Aniket Das, 19/286

This project is a bona fide work carried out by them required in partial fulfillment for the award of the degree of Bachelor of Technology under Assam Science & Technology University.

Dr. Bandana Chakrabarty

Head of the Department

Department of Chemical Engineering

Date:

Kabita Chakrabarty

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Date:

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Further we would like to extend our heartfelt gratitude to the members of the Library for their aid and supervision.

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DECLARATION

We, Chatrapati KamalNarayan Hazarika (19/279), Utpal Basumatary (19/281), Khanita Tayeng (19/282) and Aniket Das (19/286), sincerely declare that the report titled **"Production of Fromaldehyde"**:

1. The manuscript is not copied from any sources; however sources have been consulted to refer/write some pages of the report.
2. All information contained in this report correct to the best of the knowledge and belief of the author.

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ABSTRACT

In our project work we have studied the various processes available for the manufacture of formaldehyde, and have considered the process which is the most economical and viable. The material balance and the energy balance for the individual units and also the overall balance are carried out systematically along with the design of two particular equipments taking part in the plant.

PROJECT AT A GLANCE

Title: Plant design for the production of formaldehyde

Capacity: 52500 Tonnes per year of formalin (37 wt% HCHO)

Process adopted: Silver Catalyst Process

Catalyst life: 3-8 months

Equipments used: Heat exchangers, pumps, heater, reactor (with silver catalyst bed), absorber, deacidfier, distillation column, condenser, reboiler, storage tank.

Raw materials: 98.55% pure methanol, air from atmosphere.

Utilities used: Saturated steam (100°C, 1 atm), water (25°C, 1 atm)

Reaction Temperature: 680°C

Equipments designed: Storage tank for formalin and heat exchanger

Design specifications:

1. **Storage Tank:**
   Capacity = 7369.13 m^3
   D = 28.625 m
   H =11.45 m
   No. of plates = 9
2. **Heat Exchanger**:
   Type used- 1-2 Shell & tube

Shell Side	Tube Side
ID = 21$^{1/4}$ “in	Number and length = 302, 16’0” OD, BWG,
Baffle Space = 5 inch	Pitch = ¾ in, 16 BWG, 1 in tri
Passes = 2	Passes = 4

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INTRODUCTION

1.1 SUMMARY OF THE PROJECT

The main objective of this project is to conduct a comprehensive study, from a chemical point of view, that would ultimately lead to an integrated design of a plant that produces 52500 TDP/year of Formaldehyde. During this study we will consider many aspects including the entire plant's process unit design, process flow diagrams, cost estimations, operation parameters, equipment sizing, construction materials and environment/safety precautions. This project requires the theoretical and practical application of mass transfer, heat transfer, fluid dynamics, unit operations, reaction kinetics and process control. There are several tasks that are crucial to the completion of the project outlines including mass and energy balances, design of the reactor, design of heat exchangers, design of the absorber and distillation column, energy optimization, economic analysis and hazard analysis. Formaldehyde (HCHO), the target product of the project's plant, is an organic compound representing the simplest form of the aldehydes. It acts as a synthesis baseline for many other chemical compounds including phenol formaldehyde, urea formaldehyde and melamine resin. The most widely produced grade is formalin (37 wt. % formaldehyde in water) aqueous solution. In this project's study, formaldehyde is to be produced through a catalytic vapour phase oxidation reaction involving methanol and oxygen according to the following reactions:

$$CH_3OH + 1/2O_2 \rightarrow HCHO + H_2O \text{ ---(1)}$$

$$CH_3OH \rightarrow HCHO + H_2 \text{ ---------(2)}$$

First reaction is desirable which is exothermic with a selectivity of 9, while the second is an endothermic reaction. The project's target is to design a plant with a capacity of 52500 Tons/year. This plant is to include three major units; a reactor, an absorber and a distillation column. Also it includes pumps, compressors and heat exchangers. All are to be designed and operated according to this production capacity.

1.2 Properties of Formaldehyde

PHYSICAL PROPERTIES

Although formaldehyde is a gas at room temperature, it is readily soluble in water, and it is most commonly sold as a 37% solution in water called formalin or formol. In water, formaldehyde polymerizes, and formalin actually contains very little formaldehyde in the form of HCHO monomer. Usually, these solutions contain a few percent methanol to limit the extent of polymerization.

1. GENERAL PROPERTIES

Chemical formula: HCHO
Molecular mass: 30.03 amu
Appearance: Colorless Liquid
Odour: Pungent
Synonyms: Methanal, Methyl Aldehyde, Methylene Oxide.

2. GAS THERMOCHEMISTRY

Heat of Formation at 25°C = -115.9 +/- 6.3 KJ/mol

Gibb's energy at 25°C = -109.9 KJ/mol

Cp at 25°C = 35.425 J/mol.°K

Entropy at 25°C = 218.8 +/- 0.4 KJ/mol.'K

Heat of combustion at 25°C = -570.78 +/- 0.42 KJ/mol

Heat of vaporization at -19.2 °C = 23.32 KJ/mol

Heat of solution at 23°C in water = -62 KJ/mol

Heat of solution at 23°C in methanol = -62.8 KJ/mol

3. PHASE BEHAVIOUR AND PROPERTIES

Melting Point = 133.6 °K (-116.9 °C)

Boiling Point = 253.8 °K (-19.2 °C)

Flash Point = -53°C

Triple Point = -118°C

Liquid Density = 1.13 x 10° Kg/m^3

Auto-ignition Temperature = 430°C

Cubic expansion coefficient = 2.83x10°K^{-1}

Explosive limits = -0.62x 10^6

Specific Magnetic Susceptibility = 1.04

Vapor Density relative to air = 7-73%

The vapor pressure of liquid formaldehyde can be calculated for a given temperature from the following equation;

$P\ (KPa) = 10^{[3-02331429/T) + 1.75\log T - 0.0063T]}$

Generally the vapor pressure of formaldehyde at 25°C is 3890 mm Hg.

CHEMICAL PROPERTIES

Formaldehyde exhibits most of the general chemical properties of the_aldehydes, except that it is generally more reactive than other aldehydes. However,_the chemical properties of formaldehyde can be discussed as under:-

1. Formaldehyde is readily oxidized by atmospheric oxygen to form formic acid. Formaldehyde solution must be kept tightly sealed to prevent this from happening in storage.
2. Formaldehyde is a potent electrophile, and it can participate in electrophilic aromatic substitution reactions with aromatic compounds, 'and it can undergo electrophilic addition reactions with alkenes. In the presence of basic catalysts, formaldehyde undergoes a Cannizaro reaction to produce formic acid and methanol.
3. Formaldehyde reversibly polymerizes to produce its cyclic trimer, 1, 3, 5-trioxane or the linear polymer polyoxymethylene at room temperature but is stable at 80-100°C. Formation of these substances makes formaldehyde's gas behaviour differ substantially from the ideal gas law, especially at high pressure or low temperature. In water formaldehyde converts to the hydrate CHy(OH),. Thus formalin contains very little HCO. These solutions usually contain a few percent methanol to limit the extent of polymerization.

1.3 Uses of Formaldehyde

Biology

An aqueous solution of formaldehyde can be used as a disinfectant as it kills most bacteria. It is also used as a preservative in vaccinations. In medicine, formaldehyde solutions are applied topically to dry the skin, such as in the treatment of warts. Formaldehyde preserves or fixes tissue or cells by irreversibly cross-linking primary amine groups in proteins with other nearby nitrogen atoms in protein or DNA through a -CH2- linkage.

Formaldehyde based solutions are used in embalming to disinfect and temporarily preserve human remains pending final disposition. It is the ability of formaldehyde to fix the tissue that produces the tell-tale firmness of flesh in an embalmed body. While other, heavier aldehydes also produce a similar firming action, none approaches the completeness of formaldehyde. Formaldehyde is also used as a detergent in RNA gel electrophoresis, preventing RNA from forming secondary structures.

Industry

Most formaldehyde is used in the production of polymers and other chemicals.When combined with phenol, urea, or melamine, formaldehyde produces a hard thermoset resin. These resins are commonly used in permanent adhesives, such as those used in plywood or carpeting. It is used as the wet-strength resin added to sanitary paper products such as (listed in increasing concentrations injected into the paper machine headstock chest) facial tissue, table napkins, and roll towels. They are also foamed to make insulation, or cast into molded products. Production of formaldehyde resins accounts for more than half of formaldehyde consumption. Formaldehyde is still used in low concentrations for process C-41 (color negative film) stabilizer in the final wash step, as well as in the process E-6 pre-bleach step, to obviate the need for it in the final wash.

Formaldehyde is also used to make numerous other chemicals, used in personal care products such as toothpaste. Many of these are polyfunctional alcohols such as pentaerythritol, which is used to make paints and explosives. Other formaldehyde derivatives include methylene diphenyl diisocyanate, an important component in polyurethane paints and foams, and hexamine, which is used in phenol-formaldehyde resins and to make the explosive RDX.

Formaldehyde, along with 18 M (concentrated) sulfuric acid (the entire solution often called the Marquis reagent) is used as an MDMA "testing kit" by such groups as Dancesafe as well as MDMA consumers. The solution alone cannot verify the presence of MDMA, but reacts with many other chemicals that the ecstasy tablet itself may be cut with. The reaction itself produces colors which correlate with such chemicals.

Formaldehyde is ubiquitous. It is one of 27 molecules identified in interstellar space in the Milky Way. It is used in embalming fluid, as a corrosion inhibitor in oil wells, in the leather tanning process, and in paper production. Fertilizers, fiberboard, pressed wood products, plywood, germicides, fungicides, detergents, cosmetics, textiles, paints, urethane resins, water softening chemicals, tobacco, deodorants, and adhesives all contain or utilize formaldehyde. Formaldehyde is used on a tremendous scale. Billions of pounds (estimated 1.4 million tons) are consumed annually in the United States alone.

Most formaldehyde is used in the production of polymers and other chemicals. When combined with phenol, urea, or melamine, formaldehyde produces a hard thermoset resin. These resins are commonly used in permanent adhesives, such as those used in plywood or carpeting. It is used as the wet-strength resin added to sanitary paper products such as (listed in increasing concentrations injected into the paper machine headstock chest) facial tissue, table napkins, and roll towels. They are also foamed to

make insulation, or cast into molded products. Production of formaldehyde resins accounts for more than half of formaldehyde consumption.

1.4 Health effects of Formaldehyde

In high amounts formaldehyde is toxic. Because formaldehyde resins are used in many construction materials, including plywood and spray-on insulating foams, and because these resins slowly give off formaldehyde over time, formaldehyde is one of the more common indoor air pollutants. At concentrations above 0.1 ppm in air, formaldehyde can irritate the eyes and mucous membranes, resulting in watery eyes. If inhaled, formaldehyde at this concentration may cause headaches, a burning sensation in the throat, and difficulty breathing, as well as triggering or aggravating: asthma symptoms. The United States Environmental Protection Agency USEPA allows no more than 0.016 ppm formaldehyde in the air in new buildings constructed for that agency.

Large formaldehyde exposures, for example from drinking formaldehyde solutions, are potentially lethal. Formaldehyde is converted to formic acid in the body, leading to a rise in blood acidity (acidosis), rapid, shallow breathing, blurred vision or complete blindness, hypothermia, and, in the most severe cases, coma or death. People who have ingested formaldehyde require immediate medical attention.

In the body, formaldehyde can cause proteins to irreversibly bind to DNA. Laboratory animals exposed to large doses of inhaled formaldehyde over their lifetimes have developed more cancers of the nose and throat than are usual, as have workers in particle-board sawmills. However, some studies suggest that smaller concentrations of formaldehyde like those encountered in most buildings have no carcinogenic effects [citation needed]. Formaldehyde is classified as a probable human carcinogen by the U.S. Environmental Protection Agency and as having sufficient evidence that formaldehyde causes nasopharyngeal cancer in humans by the International Agency for Research on Cancer.

1.5 Storage & Handling

Where specific sources of formaldehyde occur in a workplace, ventilation is the appropriate control procedure. For example, in fabric processing, pathology laboratories, foundry molding and many particle board manufacturing plants, exhaust ventilation can maintain exposure levels well below the 8hr-TWA. For diffusion purposes, such as off-gassing particle board, urea-formaldehyde insulation or carpet, ventilation (natural or forced dilution) is the only solution. Some materials off-gas formaldehyde for periods up to 12 months after manufacture, and off-gassing problems may worsen during hot and humid weather. Significant problems occur when off-gassing materials are found in an air-conditioned space. In such cases, the fresh air make-up must be increased until the problem diminishes to tolerate

LITERATURE REVIEW OF PRODUCTION PROCESS

Formaldehyde was discovered in 1859 by a Russian chemist named Aleksandr Butlerov. Then in 1869, it was ultimately identified by the German chemist August Hofmann. The manufacture of formaldehyde started in the beginnings of the twentieth century. Between 1958 and 1968, the annual growth rate for formaldehyde production averaged to 11.7%. In the mid-1970s, the production was 54% of capacity. Annual growth rate of formaldehyde was 2.7% per year from 1988 to 1997. In 1992, formaldehyde ranked 22nd among the top 50 chemicals produced in the United States. The total annual formaldehyde capacity in 1998 was estimated by 11.3 billion pounds. Since then and the production capacity around the globe is expanding exponentially reaching a world's production of 32.5 million metric tons by 2012. Due to its relatively low costs compared to other materials, and its receptivity for reaching high purities, formaldehyde is considered one of the most widely demanded and manufactured materials in the world. It is also the centre of many chemical researches and alternative manufacture methods. This also explains the vast number of applications of this material including a building block for other organic compounds. Formaldehyde is a very versatile chemical and it is used in many industries, including - Antiseptic, Germicide and Fungicide• Purifier in Sugar Industry• Leather Tanning• Photograph Washing• Wood Working• Cabinet Making Industries• Glues and Adhesives• Paints• Explosives• Tissue Preservation• One of the main use of Formaldehyde is formaldehyde based resins. Most of the formaldehyde produced in the world is used for this. Different resins are made from formaldehyde using different substrates. One of the most popular is Urea Formaldehyde resin. Its major use is as adhesives and it is also used as a binder for glass fibre roofing materials. We will now discuss the various productions methods available.

In general two types of processes are used today.

2.1 THE SILVER CATALYST PROCESS

This process is based on partial oxidation and reduction process at 600 °C on silver grains, works with the excess of methanol above the upper explosion limit of the mixture methanol-air. In this process, formaldehyde is formed both by oxidation and by dehydrogenation reactions:

$$CH_3OH + 1/2O_2 \rightarrow HCHO + H_2O$$

$$CH_3OH \rightarrow HCHO + H_2$$

The other minor reactions that are taking place are:

$$CH_2O \rightarrow CO + H_2$$

$CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$

$CH_3OH + O_2 \rightarrow CH_2O_2 + H_2O$

The reaction occurs over a silver catalyst at typical conditions of (560- 680°C) and pressure slightly over atmosphere. Methanol conversion is 65- 75 % per pass.

2.2 THE OXIDE PROCESS

This process is based on the air oxidation of the methanol under "Lean", i.e. low methanol concentration, conditions to avoid the explosive range. In this process the methanol is produced only by the oxidation reaction:

$CH_3OH + 1/2O_2 \rightarrow HCHO + H_2O$

A small portion of formaldehyde gets oxidized further:

$HCHO+1/2\ O_2 \rightarrow CO + H_2O$

The reactions occur over a mixed oxide catalyst containing molybdenum oxide and iron oxide in the ratio 1.5 to 3. The reaction temperature is around 550°F and the reaction is slightly over atmospheric pressure. An excess air is used to ensure a near complete and to avoid the explosive range for methanol. Fresh methanol is mixed with air plus recycled gas in a steam-heated vaporizer. The effluent from this device is fed to the reactor, which is of the vertical packed tubular type. The reacting gas mixture flows downward through the tubes and transfers its heat of reaction to a circulating heat transfer medium on the shell side of the reactor. The heat transfer medium in turn vaporizes the feed water to produce steam at pressures up to about 25 atmosphere .The catalyst is granular or spherical supported Fe/Mo and has aging characteristics such that over the period of its life (12-15 months) the bed temperature must be increased from about 450 – 550 o F. The exit gases from the reactor pass through a heat recovery exchanger, where low pressure steam is generated, and thence to the absorption column where water is used as the scrubber column. The absorber can be either of the packed or the tray type. The top of the absorber is kept at a low temperature in order to ensure adequate removal of formaldehyde from the overhead gases. The bottom stream from the absorber represents the final product. Because the reaction conditions promote more formic acid than do those for the silver process, it is necessary to remove this acid by ion exchange method. A large portion of the absorber overhead is recycled back to the feed system. This permits the methanol content of the reactor feed to be as high as 9.0 volume% and causes a dilution of the gas from the absorber to the point that is not always necessary to provide further treatment of the gas discharged from the system. For this reason, the absorption column in this process is higher than that foe silver catalyst process.

SELECTION OF PROCESS

3.1 REASON FOR CHOOSING SILVER CATALYST PROCESS

Studies of the two processes based on the nominal size of 100,000,000 lb/yr of 37% formaldehyde solution showed that the silver process was far economical than the oxide process. It was found that the capital cost of the silver process was about 20% lower than the oxide process with manufacturing cost essentially the same. The conversion of methanol to formaldehyde in the improved silver process is normally between 77% and 95%, while in the older it is about 55%. So, conversion is also not a problem anymore. The most radical improvements in the silver catalyst process have been made by BASF and are now used commercially. A different form of the catalyst, a higher reaction temperature, and changes in reactor feed composition have made possible a high methanol conversion; thus, it is no longer necessary to recover unreacted methanol. Maximum size of a production unit has also been increased by these changes.

3.2 PROCESS DESCRIPTION OF SILVER CATALYST PROCESS

This process is based on partial oxidation and reduction process at 600 °C on silver grains, works with the excess of methanol above the upper explosion limit of the mixture methanol-air. In this process, formaldehyde is formed both by oxidation and by dehydrogenation reactions:

$$CH_3OH + 1/2O_2 \rightarrow HCHO + H_2O$$

$$CH_3OH \rightarrow HCHO+H_2$$

The other minor reactions that are taking place are:

$$CH_2O \rightarrow CO + H_2$$

$$CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$$

$$CH_3OH + O_2 \rightarrow CH_2O_2 + H_2O$$

The reaction occurs over a silver catalyst at typical conditions of (560-680°C) and pressure slightly over atmosphere. Methanol conversion is 65- 75 % per pass. Since the reactor feed is kept on the rich side of the explosive limit, all the oxygen is converted .Unreacted methanol is separated from the reaction mixture and recycled. A flow diagram is shown. Almost 98% fresh Methanol, which must be free from iron carbonyls and sulphur compounds (catalyst poison), is combined with recycle methanol and pumped through a steam-heated vaporizer. An additional heat exchanger for super heating the methanol may also be used. Air is drawn through a filter and compressed in a blower for feed to the process.

An air washer is provided for removal of possible catalyst poisons, and while water is usually sufficient for the scrubbing liquid, caustic solutions are sometimes needed. The washed air is pre heated and mixed with fresh feed methanol to give a combined feed temp. of about 150°C. Provision is made for the addition of up to 0.75 lb steam /lb methanol to serve as thermal ballast for reaction control. The converter consists of a feed distribution chamber, a shallow bed of catalyst, and a waste heat boiler. The catalyst is in the form of silver crystals or gauge and the catalyst bed typically is 0.5-1.0 in deep and up to 6-7 ft. in diameter. To avoid undesirable reactions it is necessary to quench the reaction product in less than about 0.02 s. Quenching is accomplished in a directly connected shell-and-tube heat exchanger where the net exothermic heat of reaction is used to generate steam. Typically the catalyst is contained in a basket resting on top of the waste heat boiler upper tube sheet, and the gases flow downward through the tubes. These gases then pass to the absorber where formaldehyde and methanol are recovered from bottom liquid. The absorber typically comprises two absorption/cooling sections with re-circulating liquid (thus providing a maximum of two theoretical stages). Either packing or trays can be used for the absorber column. The heat of solution and the residual sensible heat in the gases is removed by heat exchangers. Uncondensed material from the circulating sections flows upward through a water contracting zone for further absorption and finally leaves the top of the column and flows to a suitable device for removing residual organics and carbon monoxide. Since the gases have heating value, it is usually appropriate to add it to the fuel used for steam generation boilers. The absorber bottoms stream is pumped to the still where methanol is separated overhead and the product formaldehyde solution is the bottom stream. The water content of the bottoms is controlled by the amount of makeup water added at the top of the absorption column, and thuds there are definite upper limit for the water content in the bottoms. The methanol still typically is a tray column with conventional refluxing and re-boiling. For reduction of the bottom to 1.0 wt% methanol, 40 bubble cap trays are used. Residence time distribution can depend on the shifting equilibrium composition of the liquid, and the controlled residence time characteristics of the bubble cap tray appear advantageous. The methanol net distillate is recycled back to the fresh feed of methanol. The recycle is done in vapor phase to conserve energy. Also, some design employs vacuum distillation of methanol still to discourage the formation of higher products like acetaldehyde. If the formic acid content is higher than the distillate bottom is passed through deionizer.

MATERIAL BALANCE

4.1 **Basis**: 100 Kmol of Mixed Feed (Fresh + Recycle) per hour

Feed composition:-

$CH_3OH: O_2$ = 1: 0.4

$O_2: N_2$ = 21: 79

Water (H_2O) = **0.15%** of 100 Kmol

Formaldehyde (CH_2O) = **0.05%** of 100Kmol

Ethanol (C_2H_5OH) = **0.05%** of 100 Kmol

To prevent the accumulation of CO, CO_2 and H_2, we keep their concentrations in the recycle stream as such-

Hydrogen (H_2) = **3%** of 100 Kmol

Carbon monoxide (CO) = **0.05%** of 100 Kmol

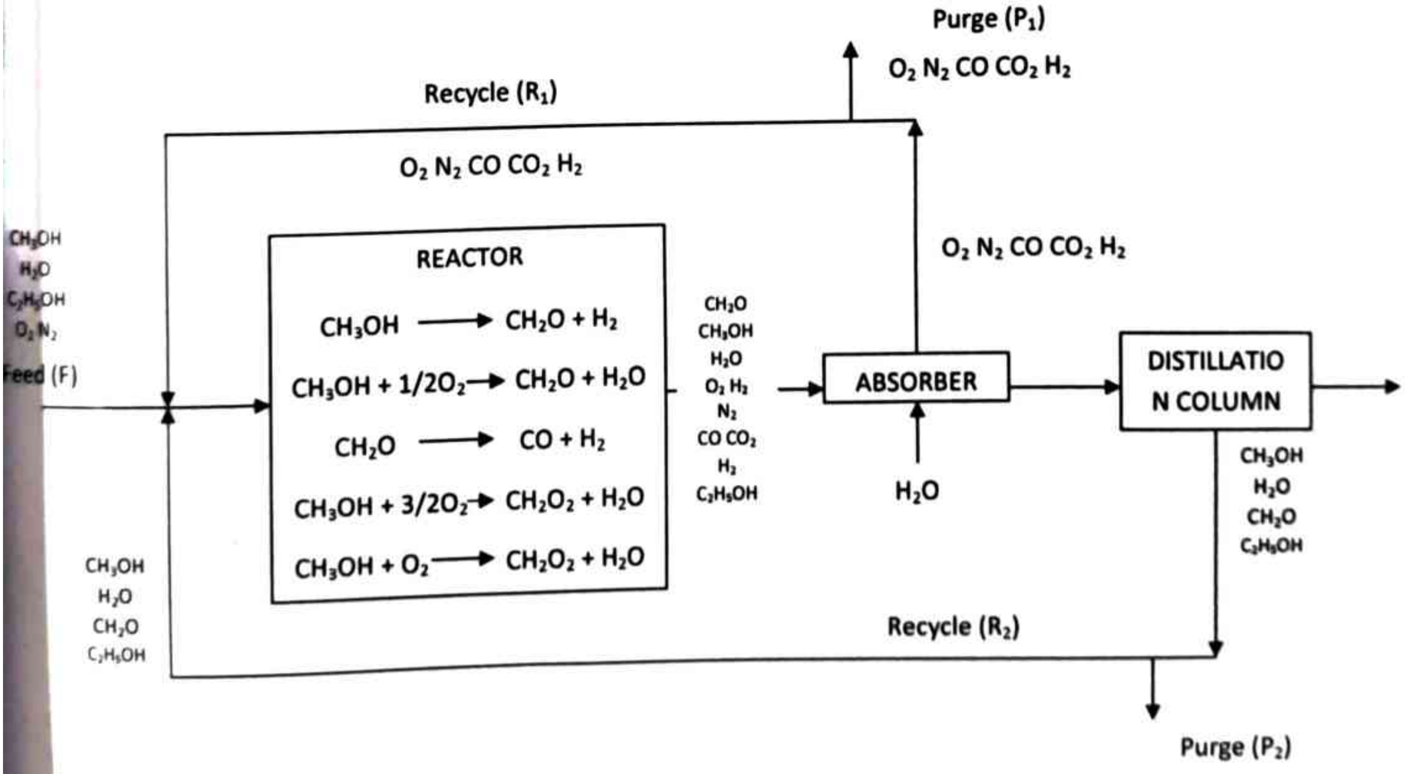
Carbon monoxide (CO_2) = **0.05%** of 100 Kmol

Therefore,

Methanol (CH_3OH) is **33.27 %** of 100 Kmol/hr

Oxygen (O_2) is **13.31%** of 100 Kmol

Nitrogen (N_2) is **50.07%** of 100 Kmol



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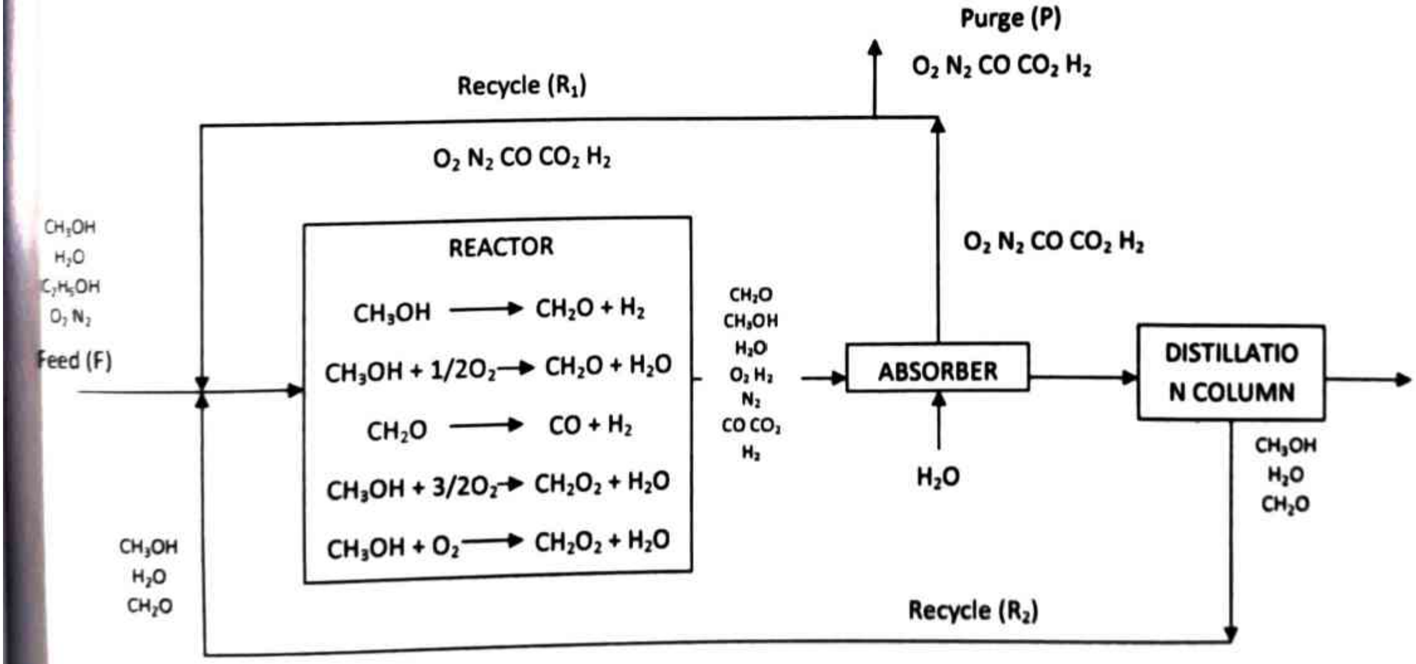


Boiling Points	**Solubility in Water**
CH_2O (-19 ^0C)	Miscible
CH_3OH (64.7 ^0C)	Miscible
CH_2O_2 (100.8 ^0C)	Slightly Miscible
C_2H_5OH (78.37 ^0C)	Miscible
H_2O (100 ^0C)	

4.2 Reactor

Reactions taking place in the reactor

$$CH_3OH \xrightarrow{\text{40 \% of } CH_3OH} CH_2O + H_2$$

$$CH_3OH + \tfrac{1}{2} O_2 \xrightarrow{\text{58 \% of } CH_3OH} CH_2O + H_2O$$

$$CH_2O \xrightarrow{\text{1 \% of } CH_2O \text{ formed}} CO + H_2$$

$$CH_3OH + 3/2\ O_2 \xrightarrow{\text{1 \% of } CH_3OH} CO_2 + 2H_2O$$

$$CH_3OH + O_2 \xrightarrow{\text{1 \% of } CH_3OH} CH_2O_2 + H_2O$$

I. **Reaction 1**

$$CH_3OH \xrightarrow{\text{Conversion = 80 \%}} CH_2O + H_2$$

Methanol reacted	= 33.27 * 0.4 * 0.8 = 10.6464 Kmol
Methanol Unreacted	= 2.6616 Kmol
Formaldehyde formed	= 10.6464 Kmol
Hydrogen formed	= 10.6464 Kmol

II. **Reaction 2**

$$CH_3OH + \tfrac{1}{2} O_2 \xrightarrow{\text{Conversion = 75 \%}} CH_2O + H_2O$$

Methanol reacted = 33.27 * 0.58 * 0.75 = 14.47245 Kmol
Methanol Unreacted = 4.82415 Kmol
Oxygen consumed = 14.47245/2 = 7.236225 Kmol
Formaldehyde formed = 14.47245 Kmol
Water formed = 14.47245 Kmol

Therefore,

Total formaldehyde formed from reaction 1 and 2 = 25.11885 Kmol

III. Reaction 3

$$\mathrm{CH_2O} \xrightarrow{\text{Conversion = 80 \%}} \mathrm{CO} + \mathrm{H_2}$$

Formaldehyde consumed = 25.11885 * 0.01 * 0.8 = 0.2009508 Kmol
Formaldehyde Unreacted = 0.0502377 Kmol
Carbon monoxide formed = 0.2009508 Kmol
Hydrogen formed = 0.2009508 Kmol

IV. Reaction 4

$$\mathrm{CH_3OH} + 3/2\ \mathrm{O_2} \xrightarrow{\text{Conversion = 90 \%}} \mathrm{CO_2} + 2\mathrm{H_2O}$$

Methanol reacted = 33.27 * 0.01 * 0.9 = 0.29943 Kmol
Methanol Unreacted = 0.03327 Kmol
Oxygen consumed = 0.29943 * 1.5 = 0.449145 Kmol
Carbon dioxide formed = 0.29943 Kmol
Water formed = 0.29943 * 2 = 0.59886 Kmol

V. Reaction 5

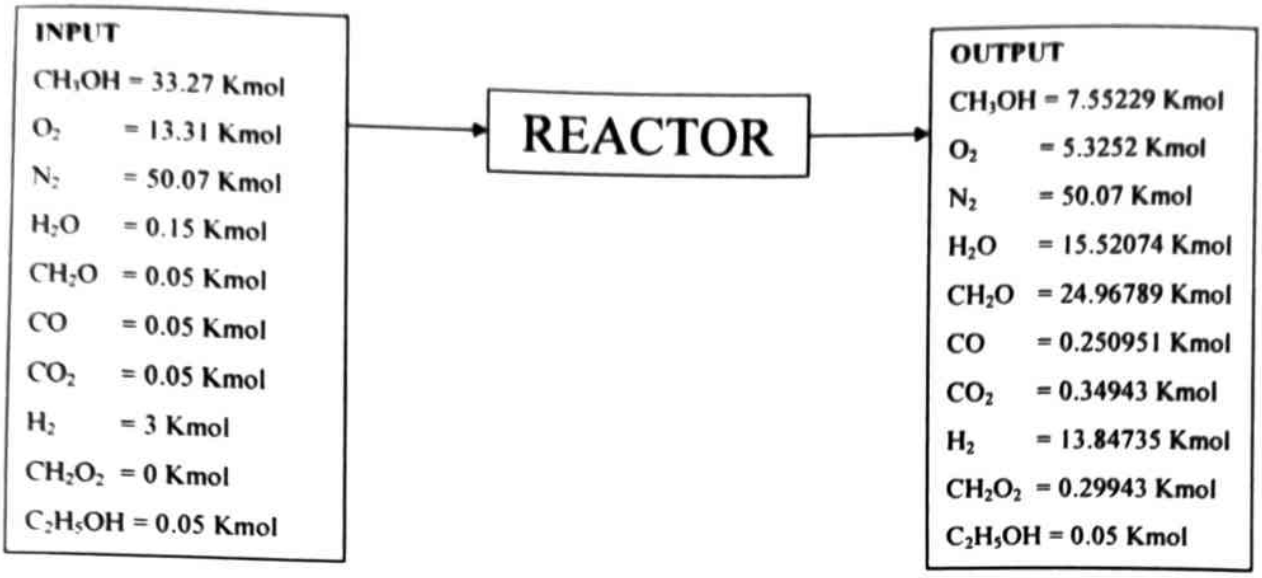
$$\mathrm{CH_3OH} + \mathrm{O_2} \xrightarrow{\text{Conversion = 90 \%}} \mathrm{CH_2O_2} + \mathrm{H_2O}$$

Methanol reacted = 33.27 * 0.01 * 0.9 = 0.29943 Kmol
Methanol Unreacted = 0.03327 Kmol
Oxygen consumed = 0.29943 Kmol
Formic acid formed = 0.29943 Kmol
Water formed = 0.29943 Kmol

Therefore,

Total Methanol Converted = 25.71771 Kmol
Total Methanol Unconverted = 7.55229 Kmol

Overall Methanol Conversion = 77.3 %



INPUT

CH_3OH = 33.27 Kmol
O_2 = 13.31 Kmol
N_2 = 50.07 Kmol
H_2O = 0.15 Kmol
CH_2O = 0.05 Kmol
CO = 0.05 Kmol
CO_2 = 0.05 Kmol
H_2 = 3 Kmol
CH_2O_2 = 0 Kmol
C_2H_5OH = 0.05 Kmol

OUTPUT

CH_3OH = 7.55229 Kmol
O_2 = 5.3252 Kmol
N_2 = 50.07 Kmol
H_2O = 15.52074 Kmol
CH_2O = 24.96789 Kmol
CO = 0.250951 Kmol
CO_2 = 0.34943 Kmol
H_2 = 13.84735 Kmol
CH_2O_2 = 0.29943 Kmol
C_2H_5OH = 0.05 Kmol

TABLE 1

MATERIAL	INPUT (Kg)	OUTPUT (Kg)
Methanol	1064.64	241.67328
Oxygen	425.92	170.4064
Nitrogen	1401.96	1401.96
Water	2.7	279.37332
Formaldehyde	1.5	749.036976
Carbon monoxide	1.4	7.0266224
Carbon dioxide	2.2	15.37492
Hydrogen	6	27.6947016
Formic acid		13.77378
Ethanol	2.3	2.3
	2908.62	2908.62

4.3 Absorber

Assumption: To prevent the accumulation of CO, CO_2 and H_2 we assume their concentration in the recycle stream to be fixed.

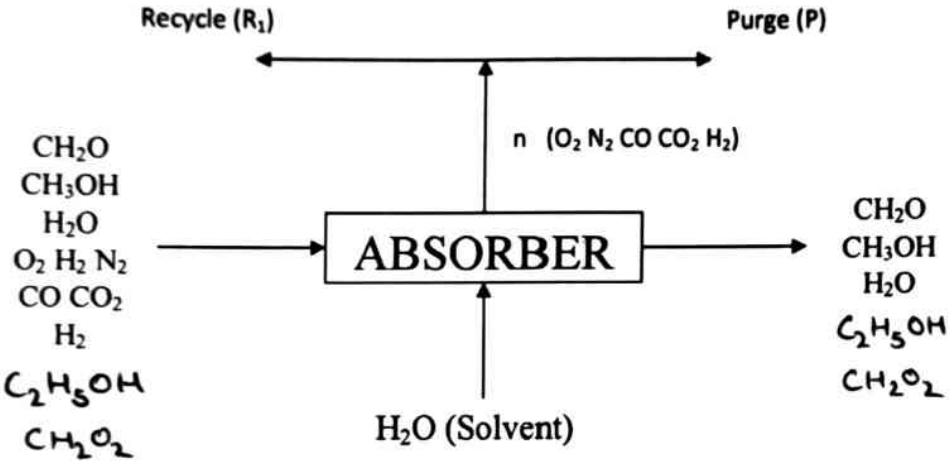
H_2 = 3 Kmol

CO = 0.05 Kmol

CO_2 = 0.05 Kmol

O_2 = 3 Kmol

N_2 = 11.28571429 Kmol



Now,

n = 5.3252 + 50.07 + 0.250951 + 0.34943 + 13.84735 = 69.870931 Kmol

R_1 = 3 + 0.05 + 0.05 + 3 + 11.28571429 = 17.38571429 Kmol

P = n – R_1 = 52.48521671 Kmol

Purge Stream composition

O_2 = 2.3252 Kmol

N_2 = 38.78428571 Kmol

H_2 = 10.84735 Kmol

CO = 0.200951 Kmol

CO_2 = 0.29943 Kmol

Therefore,

Oxygen in fresh feed = 10.31 Kmol

Nitrogen in fresh feed = 38.78428571 Kmol

To make a solution of 37 w/w % Formaldehyde Solution

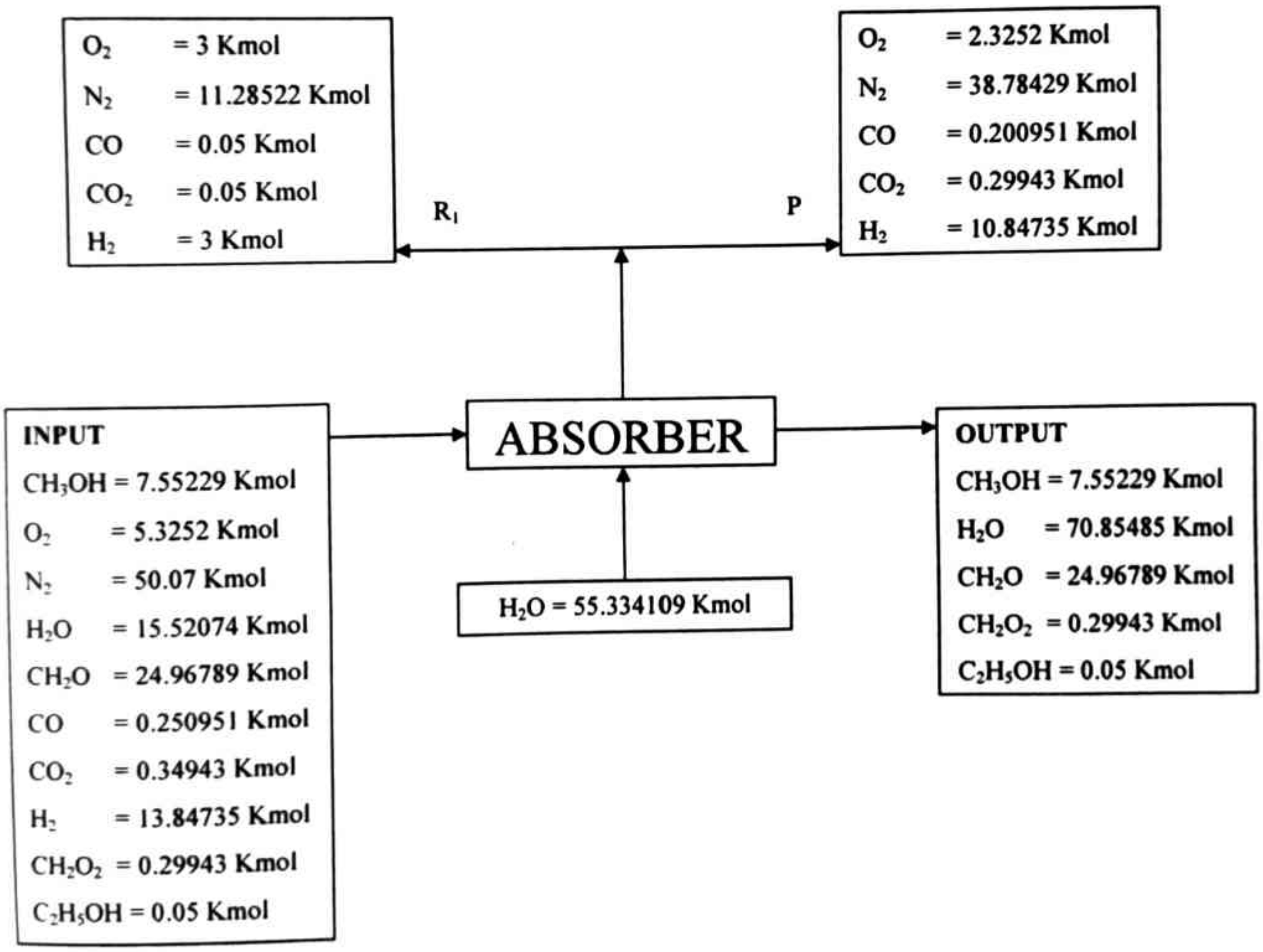
Let amount of water to be added be m kg

$$\frac{749.036976}{749.036976 + 279.37332 + m} = 0.37$$

m = 996.0139635 kg

Therefore,

Water coming out = 996.0139635 + 279.37332 = 1275.387284 kg



O_2 = 3 Kmol
N_2 = 11.28522 Kmol
CO = 0.05 Kmol
CO_2 = 0.05 Kmol
H_2 = 3 Kmol

O_2 = 2.3252 Kmol
N_2 = 38.78429 Kmol
CO = 0.200951 Kmol
CO_2 = 0.29943 Kmol
H_2 = 10.84735 Kmol

INPUT
CH_3OH = 7.55229 Kmol
O_2 = 5.3252 Kmol
N_2 = 50.07 Kmol
H_2O = 15.52074 Kmol
CH_2O = 24.96789 Kmol
CO = 0.250951 Kmol
CO_2 = 0.34943 Kmol
H_2 = 13.84735 Kmol
CH_2O_2 = 0.29943 Kmol
C_2H_5OH = 0.05 Kmol

H_2O = 55.334109 Kmol

OUTPUT
CH_3OH = 7.55229 Kmol
H_2O = 70.85485 Kmol
CH_2O = 24.96789 Kmol
CH_2O_2 = 0.29943 Kmol
C_2H_5OH = 0.05 Kmol

4.4 Distillation Column

INPUT:

CH_2O = 24.9678992 Kmol *(in the form of Formalin with 96 °C)*

CH_3OH = 7.55229 Kmol

H_2O = 70.85484911 Kmol

C_2H_5OH = 0.05 Kmol

Assuming 99% methanol recovery,

Top (R_2) = 5 Kmol Top (P_2) = 2.47677 Kmol

Bottom = 0.075522 Kmol

Assuming 99% Formaldehyde in product,

Top (R_2) = 0.05 Kmol Top (P_2) = 0.199679 Kmol

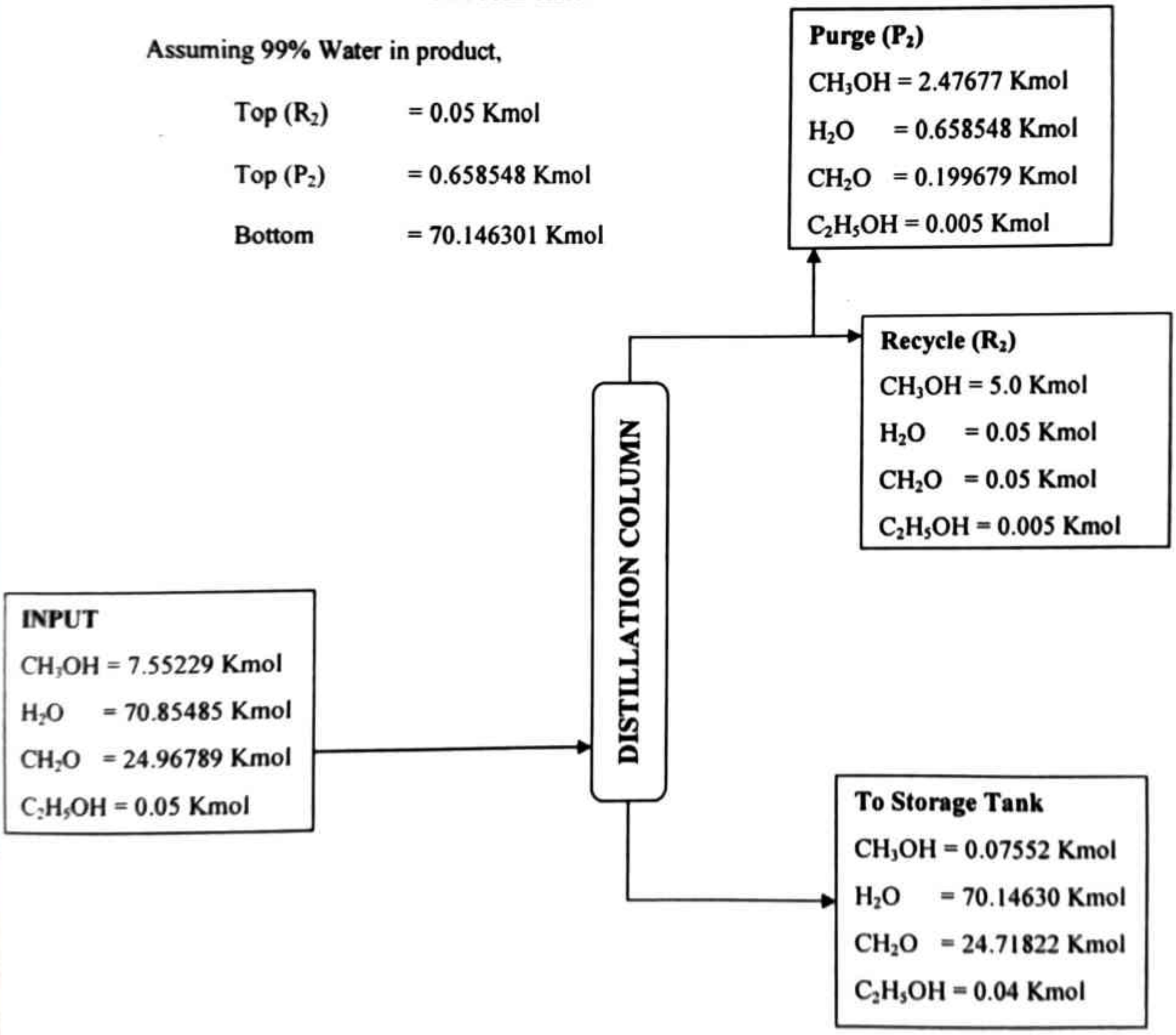
Bottom = 24.71822 Kmol

Assuming 99% Water in product,

Top (R_2) = 0.05 Kmol

Top (P_2) = 0.658548 Kmol

Bottom = 70.146301 Kmol



Assuming 80 % ethanol goes to bottom product,

Top (R_2) = 0.005 Kmol Top (P_2) = 0.005 Kmol

Bottom = 0.04 Kmol

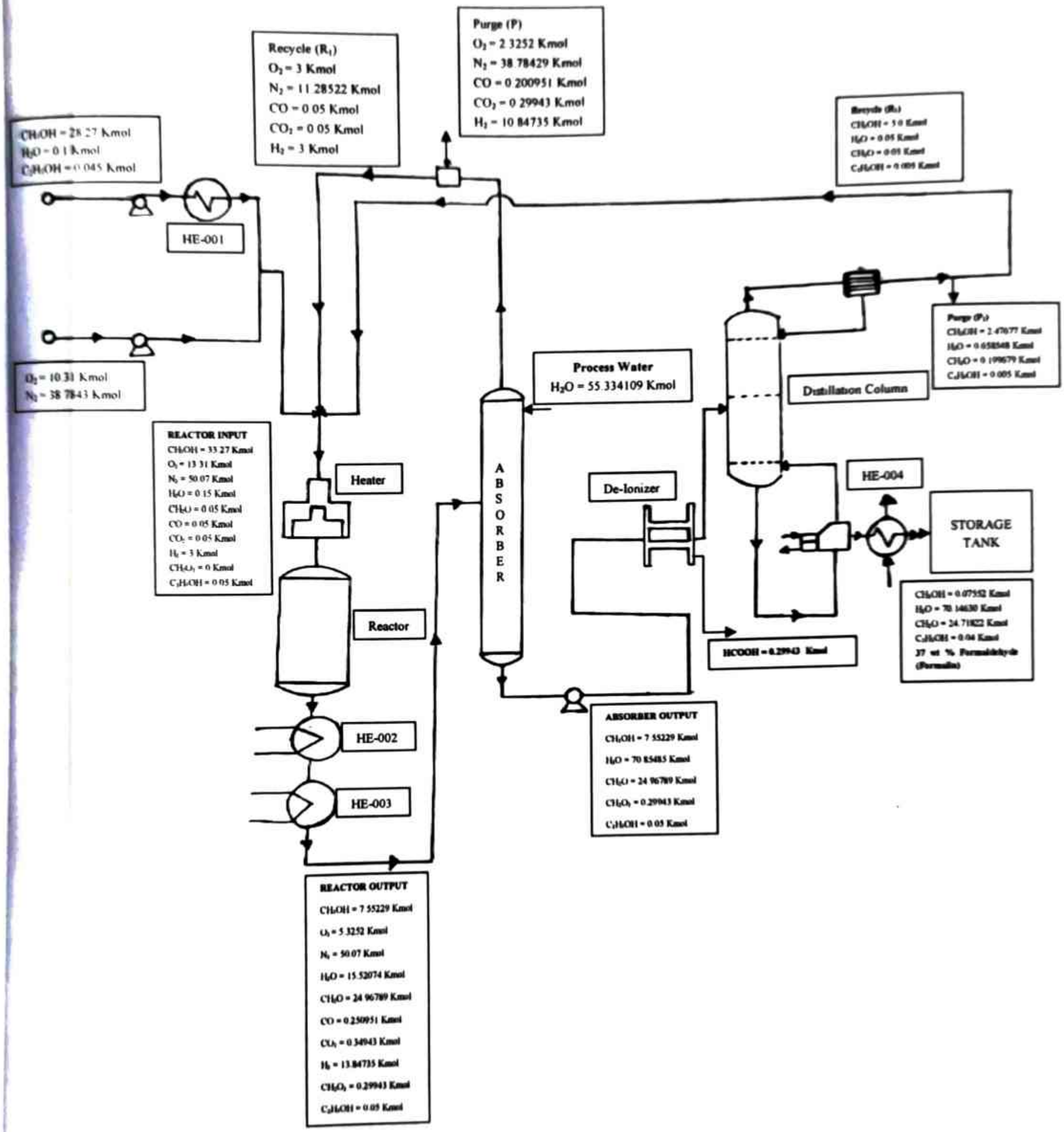
Therefore,

Fresh Methanol in feed = 28.27 Kmol

TABLE 3

MATERIAL	INPUT (Kg)	OUTPUT (Kg)	
		Top (R_2+P_2)	Bottom
CH_2O	749.036976	R_2 = 1.5 P_2 = 5.99037	741.5466
CH_3OH	241.67328	R_2 = 160 P_2 = 79.25664	2.4167328
H_2O	1275.387284	R_2 = 0.75 P_2 = 11.853864	1274.487284
C_2H_5OH	2.3	R_2 = 0.23 P_2 = 0.23	1.84
	2266.09754	2266.09754	

Material Balance Process Flow Diagram (Figure 1)



4.5 Corrected Material Balance

Multiplying Factor

Number of days in 1 year = 365 days

Number of shutdown days = 35 days

Number of working days = 330 days

Then,

Assuming a production capacity of 52500 ton per year

$$M_f = \frac{52500 * 1000}{330 * 24 * 741.5466}$$

$$= 8.86746$$

MATERIAL	INPUT (Kg)	OUTPUT (Kg)
Methanol	9445.400909	2144.106006
Oxygen	3778.728166	1511.831948
Nitrogen	12438.07696	12438.07696
Water	23.954184	2478.577745
Formaldehyde	13.30788	6645.396128
Carbon monoxide	12.420688	62.3396318
Carbon dioxide	19.518224	136.4050602
Hydrogen	53.23152	245.705177
Formic acid		122.1998743
Ethanol	20.405416	20.405416
	25805.04395	25805.04395

TABLE 4

4.5 Modified and Overall Material Balance

Multiplying Factor

Number of days in 1 year = 365 days

Number of shutdown days = 35 days

Number of working days = 330 days

Then,

Assuming a production capacity of 52500 ton per year

$$M_f = \frac{52500 \bullet 1000}{330 \bullet 24 \bullet 747.536976}$$

$$= 8.86746$$

MATERIAL	INPUT (Kg)	OUTPUT (Kg)
Methanol	9445.400909	2144.106006
Oxygen	3778.728166	1511.831948
Nitrogen	12438.07696	12438.07696
Water	23.954184	2478.577745
Formaldehyde	13.30788	6645.396128
Carbon monoxide	12.420688	62.3396318
Carbon dioxide	19.518224	136.4050602
Hydrogen	53.23152	245.705177
Formic acid		122.1998743
Ethanol	20.405416	20.405416
	25805.04395	25805.04395

TABLE 4

Distillation Column

TABLE 6.1

MATERIAL	INPUT (Kg)	TOP OUTPUT (Kg)	BOTTOM OUTPUT (Kg)
CH_3OH	2144.106006	R_2 = 1418.7936 P_2 = 702.805084	21.430281
HCHO	6645.396128	R_2 = 13.30119 P_2 = 53.119366	6575.634814
C_2H_5OH	20.405416	R_2 = 2.0395158 P_2 = 2.0395158	16.316126
H_2O	11315.14094	R_2 = 6.650595 P_2 = 105.113665	11301.465011
	20125.04849	20125.04849	

Overall Material Balance (Modified)

TABLE 6.2

INLET COMPONENTS	MASS IN (Kg)	OUTLET COMPONENT	MASS OUT (Kg)
CH_3OH	7322.732412	CH_3OH	21.441077
Air (O_2 + N_2)	12561.58757	HCHO	6632.093492
C_2H_5OH	18.36488892	C_2H_5OH	18.36488892
H_2O	15.96946863	H_2O	11307.15817
H_2O (absorbent)	8836.56319	HCOOH	122.1998743
		Tail/Off Gases (Purge)	10653.9658
	28755.22		28755.22

Distillation Column

TABLE 6.1

MATERIAL	INPUT (Kg)	TOP OUTPUT, R_2 (Kg)	BOTTOM OUTPUT (Kg)
CH_3OH	2144.106006	2122.666625	21.441077
HCHO	6645.396128	13.30789	6632.093492
C_2H_5OH	20.405416	2.0405416	18.36488892
H_2O	11315.14094	7.984734	11307.15817
	20125.04849	20125.04849	

Overall Material Balance (Modified)

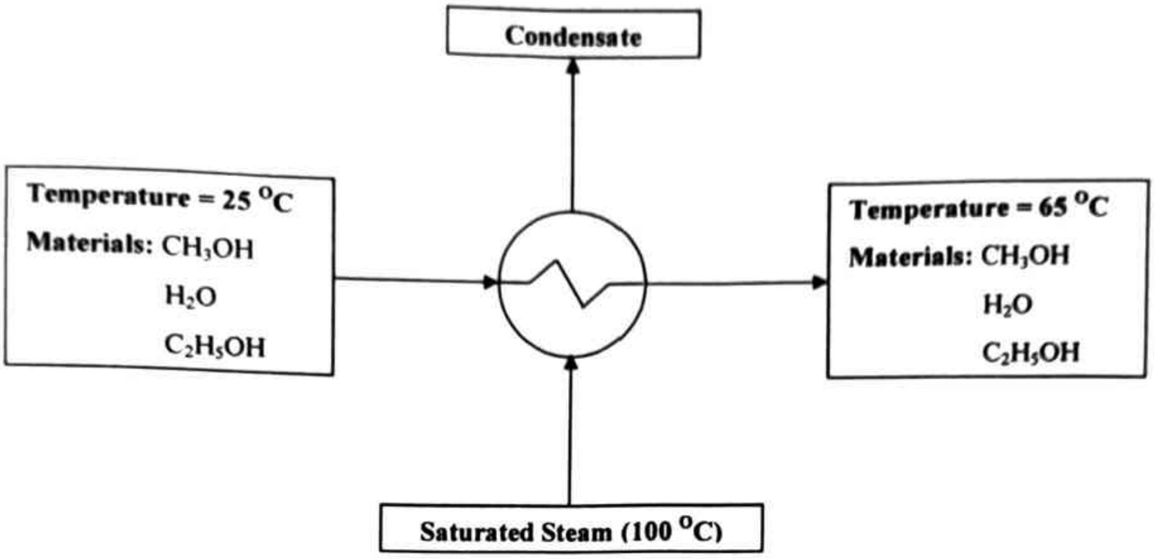
TABLE 6.2

INLET COMPONENTS	MASS IN (Kg)	OUTLET COMPONENT	MASS OUT (Kg)
CH_3OH	7322.732412	CH_3OH	21.441077
Air ($O_2 + N_2$)	12561.58757	HCHO	6632.093492
C_2H_5OH	18.36488892	C_2H_5OH	18.36488892
H_2O	15.96946863	H_2O	11307.15817
H_2O (absorbent)	8836.56319	HCOOH	122.1998743
		Tail/Off Gases (Purge)	10653.9658
	28755.22		28755.22

ENERGY BALANCE

(All data collected from Process Calculation by R K Narayan and B. Lakshmikutty)

5.1 Heat Exchanger – 1 (HE-001)



Heat capacities

$Cp_{methanol}$ (Gas) $= (18.382) + (101.564*10^{-3})T - (28.683*10^{-6})T^2$

$Cp_{ethanol}$ (Liquid) $= (-325.157) + (0.041379*10^{-2})T - (1403.1*10^{-5})T^2 + (1.7035*10^{-5})T^3$

Cp_{water} (Liquid) $= (18.2964) + (47.212*10^{-2})T - (133.38*10^{-5})T^2 + (1314.2*10^{-9})T^3$

Table 7

MATERIAL	Quantity (Kmol/hr)	ENTHALPY ENTERING ΔH_{IN}	ENTHALPY EXITING ΔH_{OUT}
Methanol	228.835498	0	437804.5275
Water	0.887192	0	2672.0699
Ethanol	0.399237	0	-19095.9585
		0	420880.639

Since, phase change occurs as Methanol (liquid) converts to Methanol (gas)

Enthalpy due to phase change (Q_v) = mL_v = 228.8354788 * 26051.2 = 5961439.346 KJ

(L_v = Latent heat of vaporization of methanol)

Therefore,

$$\Delta H_{IN} \quad + \quad Q \quad = \quad \Delta H_{OUT} \quad + \quad Q_v$$

0 + Q = 420880.639 + 5961439.346

= 6382319.985 KJ

Heat released by Steam = Q = sλ (λ = Latent heat of steam at 100 °C = 2256.9 KJ/Kg)

s = 6382319.985/2256.9 = 2826.97 Kg/hr

Hence, Steam required = 2827.9144 Kg per hour

5.2 Reactor (R-001)

Heat Capacities (Gases/vapors) *(All data collected from Process Calculation by R K Narayan and B Lakshmikutty)*

$$C_p = A + BT + CT^2$$

$C_{p\ \text{Formaldehyde}} = 4.499 + (13.9541*10^{-3})T + (3.7299*10^{-6})T^2$

$C_{p\ \text{Formic acid}} = 1.4055 + (34.632*10^{-3})T - (25.37*10^{-6})T^2$

$C_{p\ \text{Methanol}} = 18.382 + (101.564*10^{-3})T - (28.683*10^{-6})T^2$

$C_{p\ \text{Ethanol}} = 29.27 + (166.39*10^{-3})T - (49.93*10^{-6})T^2$

$C_{p\ \text{Water}} = 30.38 + (9.621*10^{-3})T - (1.185*10^{-6})T^2$

$C_{p\ \text{Oxygen}} = 25.611 + (13.26*10^{-3})T - (4.2077*10^{-6})T^2$

$C_{p\ \text{Nitrogen}} = 27.034 + (5.815*10^{-3})T - (0.2889*10^{-6})T^2$

$C_{p\ \text{Carbon monoxide}} = 26.586 + (7.582*10^{-3})T - (1.12*10^{-6})T^2$

$C_{p\ \text{Carbon dioxide}} = 26.54 + (42.454*10^{-3})T - (14.2979*10^{-6})T^2$

$C_{p\ \text{Hydrogen}} = 29.082 - (0.821*10^{-3})T + (1.9917*10^{-6})T^2$

Enthalpy of reaction

$$\Delta H_T^{\circ} = \Delta H_r^{\circ} + \Delta A\,(T) + \Delta B\,(T^2/2) + \Delta C\,(T^3/3)$$

1) Reaction 1

$$CH_3OH \xrightarrow{\text{Conversion} = 80\ \%} CH_2O + H_2$$

$\Delta H_r^{\circ} = 84$ KJ/Kmol

$\Delta A = (4.499 + 29.082) - (18.382) = 15.199$

$\Delta B = [(13.9541 - 0.821) - (101.564)]*10^{-3} = -88.4309*10^{-3}$

$\Delta C = [(3.7299 + 1.9917) - (-28.683)]*10^{-6} = 34.4046*10^{-6}$

$$\Delta H_{953\,K}^{\circ} = \Delta H_r^{\circ} + \Delta A\,(T) + \Delta B\,(T^2/2) + \Delta C\,(T^3/3)$$

$$= 84 + (15.199*953) + (-88.4309*10^{-3} * 953^2/2) + (34.4046*10^{-6} * 953^3/3)$$

$$= -15662.22973 \text{ KJ/Kmol}$$

For 80 % conversion,

$$\Delta H_{953\,K}^{\circ} = -15662.22973*0.8 = -12529.78378 \text{ KJ/Kmol}$$

2) **Reaction 2**

$$CH_3OH + \tfrac{1}{2}\,O_2 \xrightarrow{\text{Conversion} = 75\ \%} CH_2O \quad + \quad H_2O$$

$\triangle H_r^\circ = -159$ KJ/Kmol

$\triangle A = (4.499 + 30.38) - (18.382 + 2.5611/2) = 3.6915$

$\triangle B = [(13.9541 + 9.621) - (101.564 + 13.26/2)] \bullet 10^{-3} = -84.6189 \bullet 10^{-3}$

$\triangle C = [(3.7299 - 1.185) - (-28.683 - 4.2077/2)] \bullet 10^{-6} = 33.33175 \bullet 10^{-6}$

$$\triangle H_{953\,K}^\circ = \triangle H_r^\circ + \triangle A\,(T) + \triangle B\,(T^2/2) + \triangle C\,(T^3/3)$$

$$= -159 + (3.6915 \bullet 953) + (-84.6189 \bullet 10^{-3} \bullet 953^2/2) + (33.33175 \bullet 10^{-6} \bullet 953^3/3)$$

$$= -25450.35639 \text{ KJ/Kmol}$$

For 75 % conversion,

$\triangle H_{953\,K}^\circ = -25450.35639 \bullet 0.75 = -19087.76729$ KJ/Kmol

3) **Reaction 3**

$$CH_2O \xrightarrow{\text{Conversion} = 80\ \%} CO \quad + \quad H_2$$

$\triangle H_r^\circ = 12.5$ KJ/Kmol

$\triangle A = (26.586 + 29.082) - (4.499) = 51.169$

$\triangle B = [(7.582 - 0.821) - (13.9541)] \bullet 10^{-3} = -7.1931 \bullet 10^{-3}$

$\triangle C = [(-1.12 + 1.9917) - (3.7299)] \bullet 10^{-6} = -2.8582 \bullet 10^{-6}$

$$\triangle H_{953\,K}^\circ = \triangle H_r^\circ + \triangle A\,(T) + \triangle B\,(T^2/2) + \triangle C\,(T^3/3)$$

$$= 12.5 + (51.169 \bullet 953) + (-7.1931 \bullet 10^{-3} \bullet 953^2/2) + (-2.8582 \bullet 10^{-6} \bullet 953^3/3)$$

$$= 44685.52514 \text{ KJ/Kmol}$$

For 80 % conversion,

$\triangle H_{953\,K}^\circ = 44685.52514 \bullet 0.8 = 35748.42011$ KJ/Kmol

4) Reaction 4

$$CH_3OH + 3/2\,O_2 \xrightarrow{\text{Conversion} = 90\ \%} CO_2 + 2H_2O$$

$\triangle H_r^\circ = -674$ KJ/Kmol

$\triangle A = (26.54 + 2\ast 30.38) - (18.382 + 1.5\ast 25.611) = 30.5015$

$\triangle B = [(42.454 + 2\ast 9.621) - (101.564 + 1.5\ast 13.26)]\ast 10^{-3} = -59.758\ast 10^{-3}$

$\triangle C = [(14.2979 - 2\ast 1.185) - (-28.683 - 1.5\ast 4.2077)]\ast 10^{-6} = 18.32665\ast 10^{-6}$

$$\triangle H_{953\,K}^\circ = \triangle H_r^\circ + \triangle A\,(T) + \triangle B\,(T^2/2) + \triangle C\,(T^3/3)$$

$$= -674 + (30.5015\ast 953) + (-59.758\ast 10^{-3}\ast 953^2/2) + (18.32665\ast 10^{-6}\ast 953^3/3)$$

$$= 6544.9329 \text{ KJ/Kmol}$$

For 90 % conversion,

$\triangle H_{953\,K}^\circ = 6544.9329\ast 0.90 = 5890.43961$ KJ/Kmol

5) Reaction 5

$$CH_3OH + O_2 \xrightarrow{\text{Conversion} = 90\ \%} CH_2O_2 + H_2O$$

$H_r^\circ = -563.46$ KJ/Kmol

$\triangle A = (1.4055 + 30.38) - (18.382 + 25.611) = -12.2075$

$\triangle B = [(34.632 + 9.621) - (101.564 + 13.26)]\ast 10^{-3} = -70.571\ast 10^{-3}$

$\triangle C = [(-25.37 - 1.185) - (-28.683 - 4.2077)]\ast 10^{-6} = 6.3357\ast 10^{-6}$

$$\triangle H_{953\,K}^\circ = \triangle H_r^\circ + \triangle A\,(T) + \triangle B\,(T^2/2) + \triangle C\,(T^3/3)$$

$$= -563.46 + (-12.2075\ast 953) + (-70.571\ast 10^{-3}\ast 953^2/2) + (6.3357\ast 10^{-6}\ast 953^3/3)$$

$$= -42415.91777 \text{ KJ/Kmol}$$

For 90 % conversion,

$\triangle H_{953\,K}^\circ = -42415.91777\ast 0.90 = -38174.32599$ KJ/Kmol

Hence,

Total Enthalpy of reaction = Generation = - 12529.78378 – 19087.76729 + 35748.42011 + 5890.63961 – 38174.32599

= - 28152.81734 KJ

Inlet Enthalpies (Table 8)

MATERIALS	Quantity (Kmol)	ΔH_{IN}
Methanol	295.1687784	10171617.71
Oxygen	118.0852552	1960565.18
Nitrogen	444.2170343	7042107.45
Water	1.330788	24713.88
Formaldehyde	0.443596	3162.09
Carbon monoxide	0.443596	7093.33
Carbon dioxide	0.443596	10599.95
Hydrogen	26.61576	409323.16
Formic acid	0	0
Ethanol	0.443596	24615.96
		19653798.71

Outlet Enthalpies (Table 9)

MATERIALS	Quantity (Kmol)	ΔH_{IN}
Methanol	67.00331269	3057293.22
Oxygen	47.244748	993605.39
Nitrogen	444.2170343	8888289.15
Water	137.6987636	3237190.42
Formaldehyde	221.5132043	2150145.83
Carbon monoxide	2.2264154	44989.05
Carbon dioxide	3.100115005	95416.21
Hydrogen	122.8525885	2367295.17
Formic acid	2.656519	21288.74
Ethanol	0.443596	32549.97
		20888163.15

Therefore,

Heat Released from the reactor = Input – Output + Generation

= 19653798.71 – 20888163.15 – 28152.81734

= -1262517.257 KJ

Then,

Inlet temperature of Cooling Water in Water Jacket = 25 ^{o}C

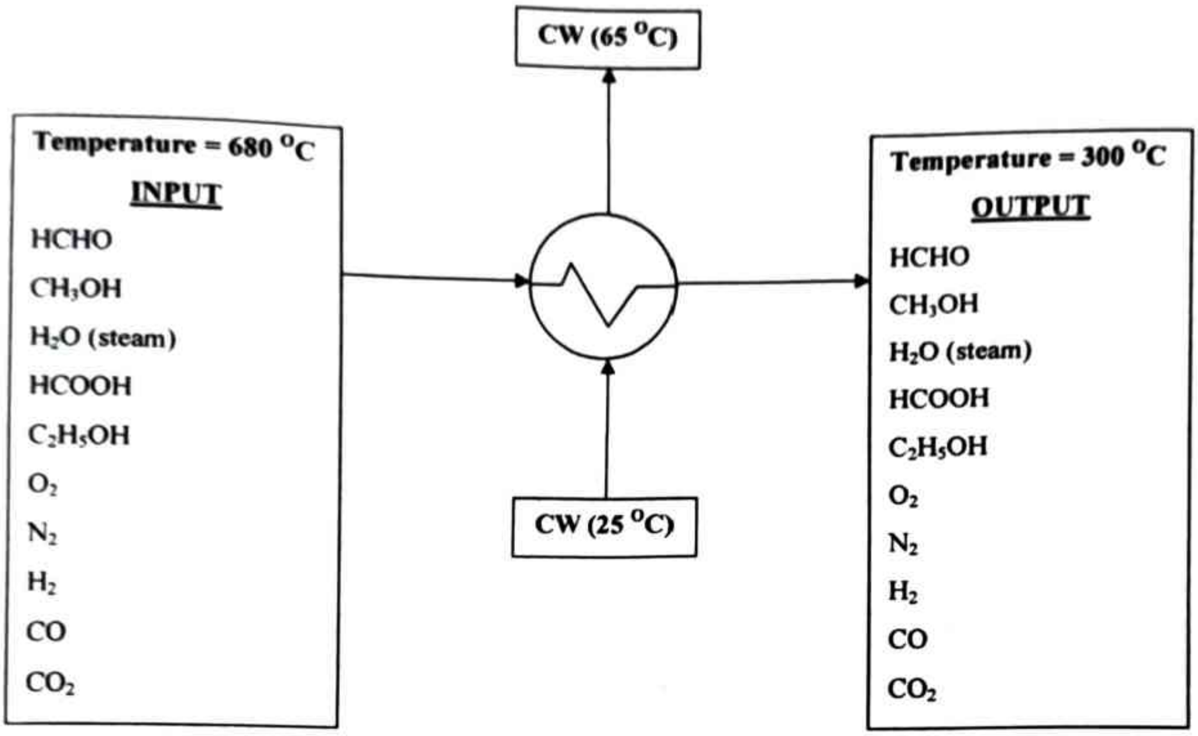
Outlet temperature of Cooling Water in Water Jacket = 65 ^{o}C

Amount of Cooling Water Required = $Q / (Cp^{*}\triangle T)$

= 1262517.257 / (4.18*40)

= 7550.9405 Kg per hour

5.3 Heat Exchanger – 2 (HE-002)



Heat capacities (all components are in vapor form)

(All data collected from Process Calculation by R.K Narayan and B. Lakshmikutty)

- $Cp_{formaldehyde} = (4.499) + (13.9541*10^{-3})T + (3.7299*10^{-6})T^2$
- $Cp_{methanol} = (18.382) + (101.564*10^{-3})T - (28.683*10^{-6})T^2$
- $Cp_{water} = (30.38) + (9.621*10^{-3})T - (1.185*10^{-6})T^2$
- $Cp_{formic\ acid} = (1.4055) + (34.632*10^{-3})T - (25.37*10^{-6})T^2$
- $Cp_{ethanol} = (29.27) + (166.39*10^{-3})T - (49.93*10^{-6})T^2$
- $Cp_{oxygen} = (25.611) + (13.26*10^{-3})T - (4.2077*10^{-6})T^2$
- $Cp_{nitrogen} = (27.034) + (5.815*10^{-3})T - (0.2889*10^{-6})T^2$
- $Cp_{hydrogen} = (29.082) - (0.821*10^{-3})T + (1.9917*10^{-6})T^2$
- $Cp_{carbon\ monoxide} = (26.586) + (7.582*10^{-3})T - (1.12*10^{-6})T^2$
- $Cp_{carbon\ dioxide} = (26.54) + (42.454*10^{-3})T - (14.2979*10^{-6})T^2$

TABLE 10

MATERIAL	Quantity (Kmol/hr)	ENTHALPY ENTERING ΔH_{IN}	ENTHALPY EXITING ΔH_{OUT}
HCHO	221.5132043	2150345.83	688774.46
CH_3OH	67.00331269	3057293.22	1050135.68
H_2O (steam)	137.6987636	3237190.42	1300272.32
HCOOH	2.656519007	21286.1	8412.01
C_2H_5OH	0.443596	32549.96	11216.69
O_2	47.24474828	993605.39	397060.18
N_2	444.2170343	8888289.15	3604910.17
H_2	122.8525885	2367295.16	983626.25
CO	2.226415421	44989.05	18164.95
CO_2	3.100115005	95417.29	36000.15
		20888261.57	8098572.86

*No phase changes occur here. So, $Q_v/Q_c=0$

Therefore,

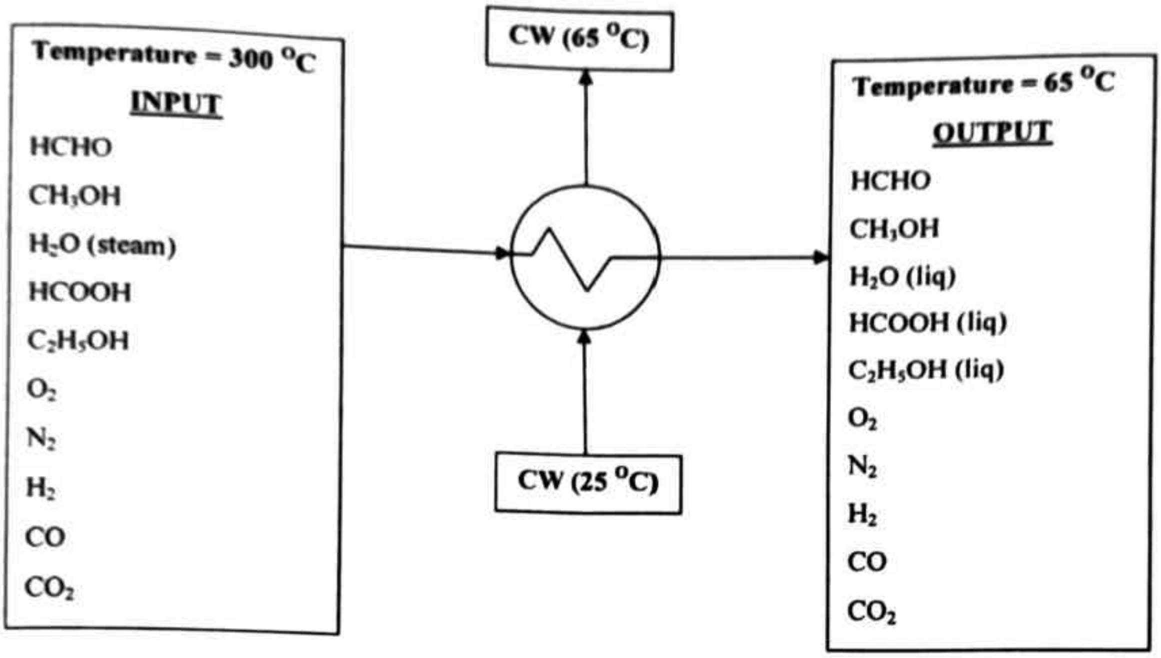
$$\Delta H_{IN} + Q = \Delta H_{OUT} + Q_{c/v}$$

$$Q = 8098572.86 - 20888261.57 = -12789688.71\text{KJ}$$

Water required = $Q / Cp_{Water}\Delta T$ ($Cp_{Water} = 4.18$ and $\Delta T = (65-25)$)

= 76493.35353 Kg per hour.

5.4 Heat Exchanger – 3 (HE-003)



Heat capacities

(All data collected from Process Calculation by R.K Narayan and B. Lakshmikutty)

6 $Cp_{formaldehyde} = (4.499) + (13.9541*10^{-3})T + (3.7299*10^{-6})T^2$

7 $Cp_{methanol} = (18.382) + (101.564*10^{-3})T - (28.683*10^{-6})T^2$

8 $Cp_{water(liquid)} = (18.2964) + (47.212*10^{-2})T - (133.88*10^{-5})T^2 + (1314.2*10^{-9})T^3$

9 $Cp_{formic\ acid(liquid)}$ = 95.4 at constant pressure & temperature range 291-385 K

10 $Cp_{ethanol(liquid)} = (-325.137) + (0.041379*10^{-2})T - (1403.1*10^{-5})T^2 + (1.7035*10^{-5})T^3$

11 $Cp_{oxygen} = (25.611) + (13.26*10^{-3})T - (4.2077*10^{-6})T^2$

12 $Cp_{nitrogen} = (27.034) + (5.815*10^{-3})T - (0.2889*10^{-6})T^2$

13 $Cp_{hydrogen} = (29.082) - (0.821*10^{-3})T + (1.9917*10^{-6})T^2$

14 $Cp_{carbon\ monoxide} = (26.586) + (7.582*10^{-3})T - (1.12*10^{-6})T^2$

15 $Cp_{carbon\ dioxide} = (26.54) + (42.454*10^{-3})T - (14.2979*10^{-6})T^2$

TABLE 11

MATERIAL	Quantity (Kmol/hr)	ENTHALPY ENTERING ΔH_{IN}	ENTHALPY EXITING ΔH_{OUT}
HCHO	221.5132043	688774.46	82527.69
CH_3OH	67.00331269	1050135.68	128043.29
H_2O (liquid)	137.6987636	1300272.32	414725.02
HCOOH (liquid)	2.656519007	8412.01	253.43
C_2H_5OH (liquid)	0.443596	11216.69	-21217.7
O_2	47.24474828	397060.18	55562.88
N_2	444.2170343	3604910.17	512696.05
H_2	122.8525885	983626.25	142620.04
CO	2.226415421	18164.95	2572.28
CO_2	3.100115005	36000.15	4785.71
		8098572.86	1322568.69

*Phase changes occur for H_2O, HCOOH & C_2H_5OH.

Q_c for H_2O at 65 ^{O}C=5601.586 KJ per mol

Q_c for HCOOH at 65 ^{O}C=58.6559 KJ per mol

Q_c for C_2H_5OH at 65 ^{O}C=17.26 KJ per mol

Total Q_C =5677.502 KJ per mol

Therefore,

$$\Delta H_{IN} \quad + \quad Q \quad = \quad \Delta H_{OUT} \quad + \quad Q_{c/v}$$

Q = 1322568.69 + 5677.502 - 8098572.86

Q = -60770326.668 KJ

Water required = $Q / Cp_{Water} \Delta T$ (Cp_{Water} = 4.18 and ΔT= (65-25))

= 40492.3845 Kg per hour.

5.5 ABSORBER

Assuming heat of mixing and heat of absorption is negligible.

Amount of H_2O supplied for absorption = 8836.56319 Kg/hr = 490.9201772 Kmol/hr

ΔH_{IN} for Solvent = 0 KJ

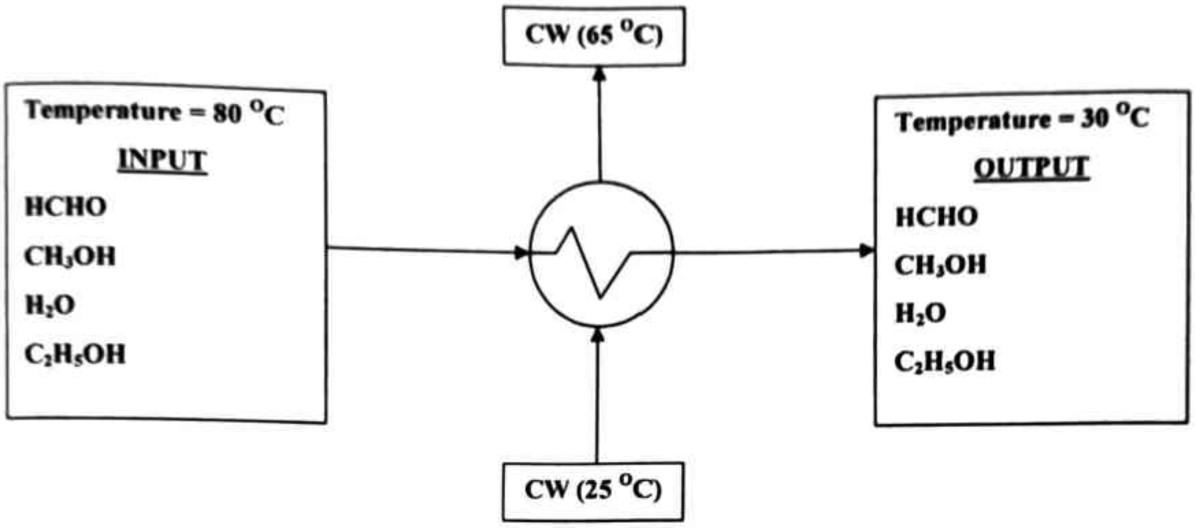
TABLE 12

MATERIAL	Quantity (Kmol/hr)	ENTHALPY ENTERING ΔH_{IN}	ENTHALPY EXITING ΔH_{OUT}
HCHO	221.5132043	82527.69	280761.5
CH_3OH	67.00331269	128043.29	-10777288.46
H_2O	137.6987636	414725.02	155008.16
H_2O(Solvent)	490.9201772	0	552631.204
HCOOH	2.656519007	253.43	253.43
C_2H_5OH	0.443596	-21217.7	-7643.97
O_2	47.24474828	55562.88	Tail/off gas =11118846.83
N_2	444.2170343	512696.05	
H_2	122.8525885	142620.04	
CO	2.226415421	2572.28	
CO_2	3.100115005	4785.71	
		1322568.69	1322568.69

***Phase change occurs for methanol. Cp value has been changed accordingly.**

$Cp_{methanol\ (liquid)} = (-259.25) + (0.03358*10^{-2})T - (11639*10^{-5})T^2 + (1.4052*10^{-5})T^3$

5.6 Heat Exchanger – 4 (HE-004)



<u>Heat capacities</u> *(All data collected from Process Calculation by R.K Narayan and B. Lakshmikutty)*

$Cp_{methanol} = (-259.25) + (0.03358*10^{-2})T - (11639*10^{-5})T^2 + (1.4052*10^{-5})T^3$

$Cp_{ethanol} = (-325.137) + (0.041379*10^{-2})T - (1403.1*10^{-5})T^2 + (1.7035*10^{-5})T^3$

$Cp_{water} = (18.2964) + (47.212*10^{-2})T - (133.88*10^{-5})T^2 + (1314.2*10^{-9})T^3$

$Cp_{formaldehyde} = (25.099) + (79.3671*10^{-2})T - (382.691*10^{-5})T^2 + (6104.92*10^{-9})T^3$

TABLE 13

MATERIAL	Quantity (Kmol/hr)	ENTHALPY ENTERING ΔH_{IN}	ENTHALPY EXITING ΔH_{OUT}
CH_3OH	0.67	-447062.82	-34800.16
H_2O	628.175	2606210.87	235362.34
HCHO	221.07	1082795.64	92504.62
C_2H_5OH	0.399	-26864.56	-2255.22
		3215079.13	290811.58

*No phase changes occur here. So, $Q_v/Q_c = 0$

Therefore,

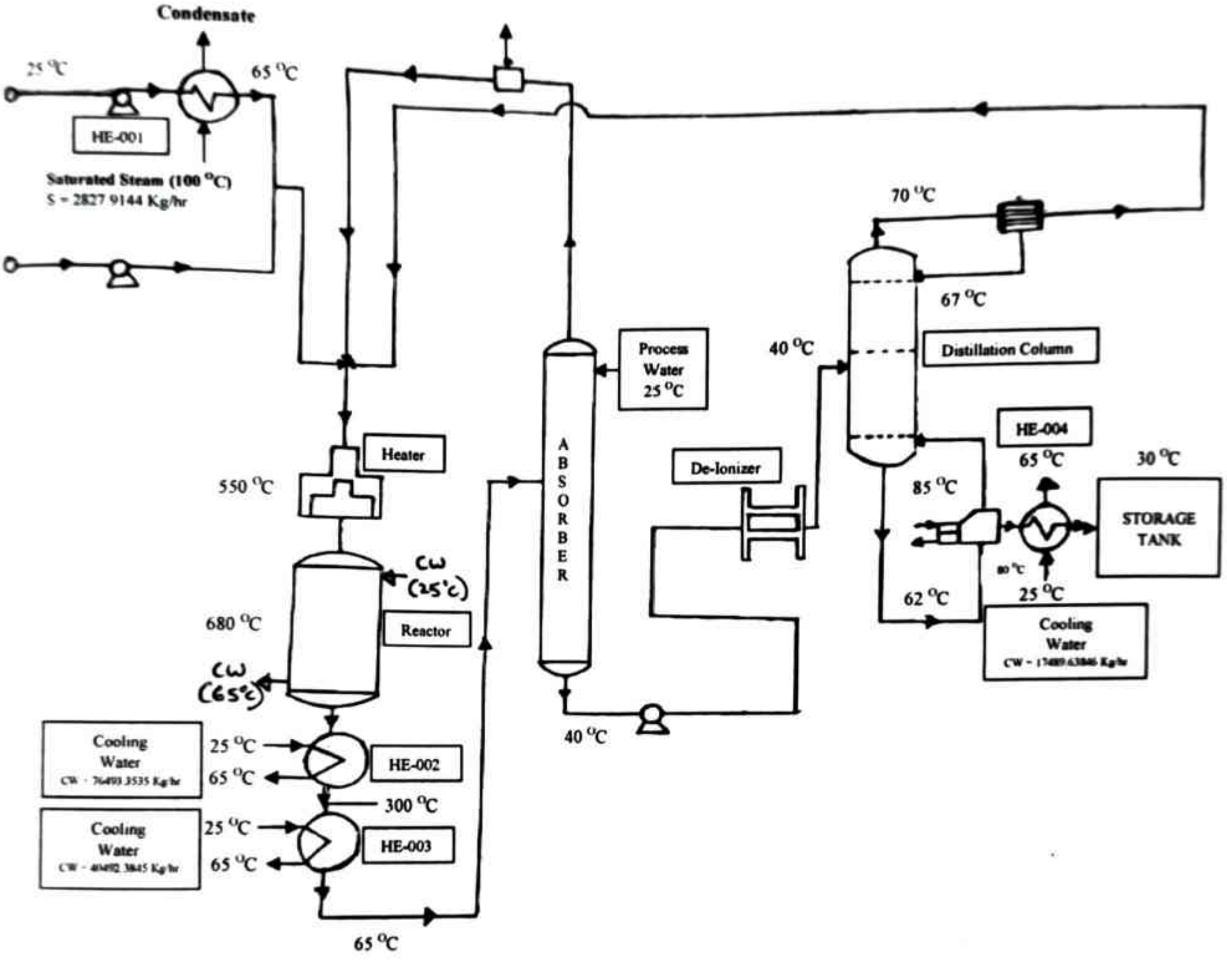
$$H_{IN} \quad + \quad Q \quad = \quad H_{OUT} \quad + \quad Q_{e/v}$$

$$Q \quad = 290811.58 - 3215079.13 \quad = -2924267.55 \text{ KJ}$$

Water required = $Q / Cp_{Water} \Delta T$ [$Cp_{Water} = 4.18$ and $\Delta T = (65-25)$]

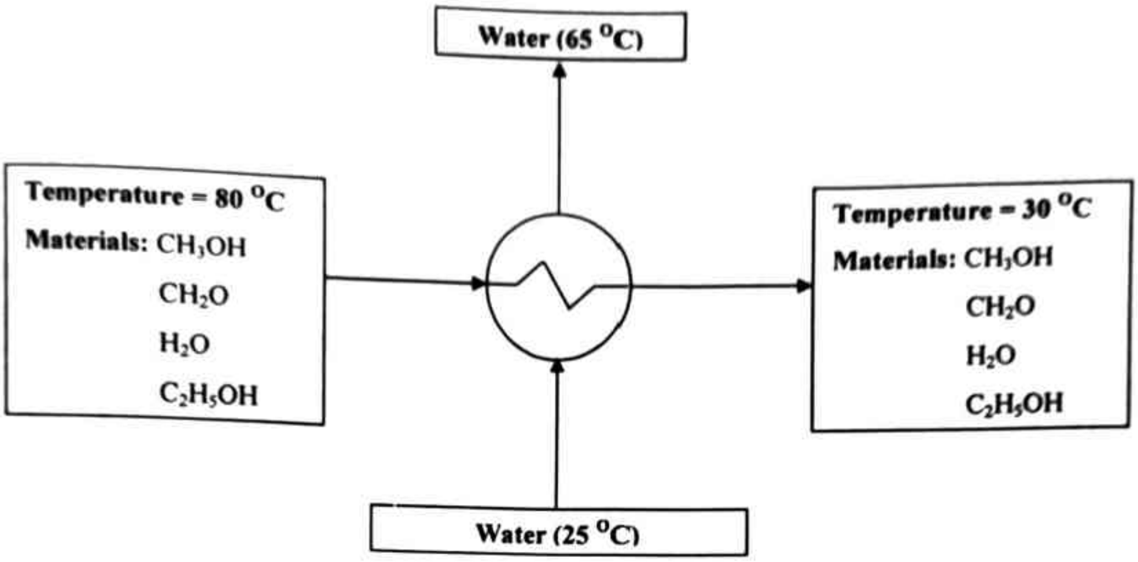
= 17489.63846 Kg per hour.

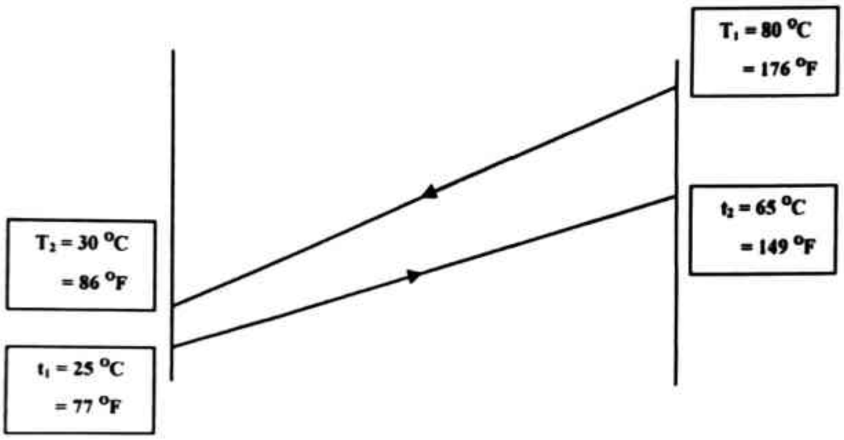
Energy Balance Process Flow Diagram (Figure 3)



DESIGN

6.6 Heat Exchanger-4 (HE-004)





(All values acquired from Process Heat Transfer by D.Q Kern)

STEP-1 Heat Balance *(from Energy Balance data of HE-004)*

$Q_{hot} = Q_{cold}$

2924267.55 KJ = 2924267.55 KJ

2771670.8482 Btu/hr = 2771670.8482 Btu/hr

STEP-2

$$\text{LMTD} = \frac{\triangle T_2 - \triangle T_1}{\ln(\triangle T_2/\triangle T_1)} = 48.384\ ^{O}F$$

$R = (T_1 - T_2)/(t_2 - t_1) = (176 - 86)/(149 - 77) = 1.25$

$S = (t_2 - t_1)/(T_1 - t_1) = (149 - 77)/(176 - 77) = 0.727$

Correction Factor (F_t) = 0.81 *(from fig 28)*

Therefore,

$\triangle t = \text{LMTD} \cdot F_t = 39.19204\ ^{O}F$

STEP-3 **Area Calculation** [$U_D = 150$] *(Table 8)*

$A = Q/(U_D \cdot \triangle t) = 2771670.848/(150 \cdot 39.19204) = 471.480\ ft^2 > 200\ ft^2$

Hence, 1-2 Shell and Tube H.E is used.

Assumptions *(from Table 1)*

Shell Side	Tube Side
ID = $21^{1/4}$ in	Number and length = 302, 16'0" OD, BWG, Pitch = ¾ in, 16 BWG, 1 in tri
Baffle Space = 5 inch	
Passes = 2	Passes = 4

STEP-4

Average Temperature / Caloric Temperature

Hot stream (at cold end T = 86 ^{O}F)		Cold stream (at cold end T = 77 ^{O}F)	
(From fig 14)		*(From fig 14)*	
$\mu_{methanol}$	= 0.62 Cp	$\mu_{methanol}$	= 0.68 Cp
μ_{water}	= 0.86 Cp	μ_{water}	= 0.88 Cp
$\mu_{Formaldehyde}$	= 0.12 Cp	$\mu_{Formaldehyde}$	= 0.1421 Cp
$\mu_{ethanol}$	= 1.2 Cp	$\mu_{ethanol}$	= 1.4 Cp
$\mu_{mixture}$	$= \frac{0.62 + 0.86 + 0.12 + 1.2}{4}$	$\mu_{mixture}$	$= \frac{0.68 + 0.88 + 0.1421 + 1.4}{4}$
	= 0.7 Cp < 1 Cp		= 0.775 Cp < 1 Cp

Therefore, Average Temperature can be used.

$T_{Average}$ = (86 + 176) / 2 = 131 °F

$t_{Average}$ = (77 + 149) / 2 = 113 °F

STEP-5

Property Table (Table 14.1)

Hot Stream (T = 131 °F)	**Cold Stream (T = 113 °F)**
From fig 14 $\mu_{methanol}$ = 0.36 Cp μ_{water} = 0.504 Cp $\mu_{Formaldehyde}$ = 0.56 Cp $\mu_{ethanol}$ = 0.61 Cp $\mu_{mixture}$ = 0.5085 Cp	*From fig 14* $\mu_{methanol}$ = 0.407 Cp μ_{water} = 0.59 Cp $\mu_{Formaldehyde}$ = 0.76 Cp $\mu_{ethanol}$ = 0.78 Cp $\mu_{mixture}$ = 0.63425 Cp
Cp_{water} = 0.97 *(fig 2)* $Cp_{formaldehyde}$ = 0.8 $Cp_{ethanol}$ = 0.8 $Cp_{methanol}$ = 1.85 *{ From Process Calculation by R.K Narayan and B. Lakshmikutty }* $Cp_{mixture}$ = 1.105 Btu/lb	Cp_{water} = 0.95 *(fig 2)* $Cp_{formaldehyde}$ = 0.73 $Cp_{ethanol}$ = 0.79 $Cp_{methanol}$ = 0.98 *{ From Process Calculation by R.K Narayan and B. Lakshmikutty }* $Cp_{mixture}$ = 0.85 Btu/lb
From Table 4 $k_{ethanol}$ = 0.088 k_{water} = 0.372 $k_{methanol}$ = 0.118 $k_{formaldehyde}$ = 0.107 *(from NIST Webbook)* k_{min} = 0.17125	*From Table 4* $k_{ethanol}$ = 0.9 k_{water} = 0.361 $k_{methanol}$ = 0.212 $k_{formaldehyde}$ = 0.202 *(from NIST Webbook)* k_{min} = 0.41875
From Table 6 $S_{ethanol}$ = 0.81 S_{water} = 0.98 $S_{methanol}$ = 0.82 $S_{formaldehyde}$ = 0.79 S_{min} = 0.85 ρ_{min} = 0.85*62.5 = 53.125 lb/ft^3	*From Table 6* $S_{ethanol}$ = 0.79 S_{water} = 0.96 $S_{methanol}$ = 0.79 $S_{formaldehyde}$ = 0.77 S_{min} = 0.8275 ρ_{min} = 0.8275*62.5 = 51.718 lb/ft^3

STEP-6

h_o and h_i calculation (TABLE 14.2)

Shell Side (Hot Stream)	Tube Side (Cold Stream)
$a_s = (ID*c'B) / (144*P_T)$ $= (21.25*0.25*5) / (144*1)$ $= 0.1844\ ft^2$	$a_t' = 0.302$ $a_t = (N_t*a_s) / (144*u) = (302*0.302) / (144*16)$ $= 0.0395\ ft^2$
$G_s = m_h / a_s = 214988.407$ *(m_h from energy balance)*	$G_t = m_c / a_t = 1003642.086$ *(m_c from energy balance)*
$D_e = 0.73/12 = 0.061$ *(fig 28)* $Re_s = (D_e*G_s) / \mu = 214988.407*0.061/0.5085$ $= 25790.1531$	$D_i = 0.62/12 = 0.051$ ft (table 10) $Re_t = (D_i*G_t) / \mu = 1003642.086*0.051/0.63425$ $= 80702.786$
jH = 98 *(From Fig 24)*	jH = 211 *(From Fig 26)*
$h_o = (jH*k / D)*(Cp*\mu/k)^{1/3} = 406.675$	$h_i = (jH*k / D)*(Cp*\mu/k)^{1/3} = 1879.494$ $h_{io} = h_i * (ID/OD) = 1474.95529$

STEP-7

U_c Calculation

$$U_c = (h_{io} * h_o) / (h_{io} + h_o) = (406.675*1474.95529) / (406.675 + 1474.95529)$$

$$= 318.78071\ Btu/ft^2\ {}^{O}F$$

$$U_c > U_D$$

STEP-8

Dirt Factor calculation

$$R_d = 1/U_D - 1/U_c = 1/150 - 1/1104 = 0.003529$$

STEP-9

Pressure drop Calculation (TABLE 14.3)

Shell Side	Tube Side
f = 0.0017 *(From Fig 29)*	f = 0.00016 *(From Fig 28)*
$D_e' = 21.25/12 = 1.77$ ft	$\triangle P_t = \frac{fG^2L_n}{(5.22*10^{10})D_s\phi_t} = 3.491$ psi
$N + 1 = 12(L/B) = 39$	$\triangle P_T = \triangle P_t + \triangle P_r$
$\triangle P = \frac{fG^2(N+1)D_e'}{(5.22*10^{10})s\phi_s D_e}$	$v^2/2g' = 0.12$ *(From Fig 27)*

$= 1.90857$ psi < 10 psi	$\triangle P_r = 4nv^2/s2g' = (4*4*0.12)/(0.85) = 2.258$ psi $\triangle P_T = 3.491 + 2.258 = 5.748$ psi < 10 psi

Therefore,

Allowable pressure drop is 10 psi.

6.2 Storage Tank

Assumptions

Let C_1 = Annual cost of shell/unit area.
Let C_2 = Annual cost of bottom/unit area.
Let C_3 = Annual cost of roof/unit area.
Let C_4 = Annual cost of foundation/unit area.
Let C_5 = Annual cost of installation.

The optimum diameter to height ratio,
For large tank = $D/H = 4C_1/(C_2 + C_3 + C_4 + C_5)$
For small tank = $D/H = 2C_1/(C_2 + C_3 + C_4 + C_5)$
Where,
$C_1 = 2C_2$
$C_3 = 1.5C_2$
$C_4 + C_5 = 0.5C_2$
Let,

t = Minimum thickness of shell plate in mm
H = Height of the tank in m.
D = Diameter of the tank in m/
G = specific gravity of liquid to be stored (assume 1)
S = allowable stress in kgf/cm^2
E = Joint efficiency factor
W = width of each plate in m.
n = no. of thickness sections

Consider corrosion allowance 1.5mm (for stainless steel/carbon steel/cast iron)
Let us assume the material to be IS: 2002-1962, grade 2B steel **(acc. to Appendix A, table A-1; Process Equipment Design-mechanical aspects; B C Bhattacharjee)**
$S = 12.1\ kgf/mm^2$ (upto 250°C)
$S = 1210\ kgf/cm^2$

BASIS: 15 days of operation.

1. For H_2O

Mass= 11307.15817 Kg (from corrected material balance)

= (11307.15817*15*24) =4070576.941Kg

Density=1000 Kg/m^3

Volume=4070.577 m^3

2. For HCHO

Mass= 6632.093492 Kg (from corrected material balance)

= (6632.093492 *15*24) =2387553.657Kg

Density=815 Kg/m^3

Volume=2929.514 m^3

3. For CH_3OH

Mass= 21.441077 Kg (from corrected material balance)

= (21.441077 *15*24) =7718.78772Kg

Density=792 Kg/m^3

Volume=9.746m^3

4. For C_2H_5OH

Mass= 18.36488892Kg (from corrected material balance)

= (18.36488892*15*24) =6611.3600011Kg

Density=789 Kg/m^3

Volume=8.38 m^3

TOTAL VOLUME, $V_T = V_{H20} + V_{HCHO} + V_{CH3OH} + V_{C2H5OH}$

$V_T = 7012.217\ m^3$

Volume allowance = 5%

Actual volume, $V = V_T + (0.05 * V_T) = 7369.13\ m^3$

NOW, Let us assume small tank.

First,

For small tank = $D/H = 2C_1/(C_2 + C_3 + C_4 + C_5)$

Where,

$(C_1=2C_2,\ C_3=1.5C_2,\ C_4 + C_5=0.5C_2)$

$D = 1.25H$

Then, $V = (\pi/4)*(D^2H)$

We have V=7369.13 m^3 from calculations.

Putting values of V and D, we find out H.

$H = 18.18m = 59.646\ ft$

So, $D = 1.25 * 18.18 = 22.725 = 74.56\ ft$

Now, we find the value of $D*(H-1) = 74.56 *(59.646 - 1) = 4372.6$ which is >1720.

Therefore, our assumption for considering small tank is incorrect.

NOW, Let us assume large tank.

First,

For large tank = $D/H = 4C_1/ (C_2 + C_3 + C_4 + C_5)$

Where,

$(C_1=2C_2, C_3=1.5C_2, C_4 + C_5=0.5C_2)$

$D = 2.5H$

Then, $V= (\pi/4)*(D^2H)$

We have $V=7369.13\ m^3$ from calculations.

Putting values of V and D, we find out H.

$H = 11.45m = 37.6\ ft$

So, $D = 2.5*11.45 = 28.625m = 93.9\ ft$

Now, we find the value of $D*(H-1) = 93.9 *(37.6 - 1) = 3436.74$ which is >1720.

Therefore, our assumption for considering large tank is correct.

We have, $D = 28.625m$

(For this nominal tank diameter, t_{min}=6mm acc. To Clause 6.3.3.2, IS: 803, 1976; Process Equipment Design-mechanical aspects; B C Bhattacharjee)

$H = 11.45m$

Assuming Double-welded butt joint (DWBJ), we have E=0.85 (joint efficiency factor)

Let us assume no. of plates to be 9(n).

Therefore length, $L= (\pi * D)-(2*n*10^{-3})/n = 9.98m$ **(between 6m-10m; easily available acc. To Appendix B, table B-1; Process Equipment Design-mechanical aspects; B C Bhattacharjee)**

Width of the plates, $W = H/n = 11.45/9 = 1.272m$

W= 1272mm which is approximately equal to 1250 mm

(acc. to Appendix B, table B-1; Process Equipment Design-mechanical aspects; B C Bhattacharjee)

Therefore, $W_{standard}$ = 1.25m.

Now, we will calculate the thickness for each plate.

i. t_1 = 50*D*G*(H-0.3)/SE

t_1 = 15.52mm

t_{1f} = 15.52 + 1.5 = 17.02 mm (1.5mm is the corrosion allowance)

t_{1std} = 18mm > t_{min} (6mm)

(acc. to Appendix B, table B-1; Process Equipment Design-mechanical aspects; B C Bhattacharjee)

ii. H_2 = 11.45 – 1.25 = 10.2m

t_2 = 50*D*G*(H-0.3)/SE

t_2 = 13.8mm

t_{2f} = 13.8 + 1.5 = 15.3 mm

t_{2std} = 16mm > t_{min} (6mm)

iii. H_3 = 10.2 – 1.25 = 8.95m

t_3 = 50*D*G*(H-0.3)/SE

t_3 = 12.04mm

t_{3f} = 12.04 + 1.5 = 13.54 mm

t_{3std} = 14mm > t_{min} (6mm)

iv. H_4 = 8.95 – 1.25 = 7.7m

t_4 = 50*D*G*(H-0.3)/SE

t_4 = 10.3mm

t_{4f} = 10.3 + 1.5 = 11.8 mm

t_{4std} = 12mm > t_{min} (6mm)

v. H_5 = 7.7 – 1.25 = 6.45m

t_5 = 50*D*G*(H-0.3)/SE

t_5 = 8.56mm

t_{5f} = 8.56 + 1.5 = 10.06 mm

t_{5std} = 10mm > t_{min} (6mm)

vi. $H_6 = 6.45 - 1.25 = 5.2m$

$t_6 = 50*D*G*(H-0.3)/SE$

$t_6 = 6.82mm$

$t_{6f} = 6.82 + 1.5 = 8.32$ mm

$t_{6std} = 8mm > t_{min}$ (6mm)

vii. $H_7 = 5.2 - 1.25 = 3.95m$

$t_7 = 50*D*G*(H-0.3)/SE$

$t_7 = 5.08mm$

$t_{7f} = 5.08 + 1.5 = 6.58$ mm

$t_{7std} = 7mm > t_{min}$ (6mm)

viii. $H_8 = 3.95 - 1.25 = 2.7m$

$t_8 = 50*D*G*(H-0.3)/SE$

$t_8 = 3.34mm$

$t_{8f} = 3.34 + 1.5 = 4.84$ mm

$t_{8std} = 6$ mm

ix. $H_9 = 2.7 - 1.25 = 1.45m$

$t_9 = 50*D*G*(H-0.3)/SE$

$t_9 = 1.6$ mm

$t_{9f} = 1.6 + 1.5 = 3.1$ mm

$t_{9std} = 6mm$

*t_8 and t_9 standard thickness value will 6mm **(in ref: Clause 6.3.3.2, IS: 803, 1976; Process Equipment Design-mechanical aspects; B C Bhattacharjee)**

TABLE 15

Thickness section	Thickness, t (mm)	Thickness with corrosion allowance, t_f (mm)	Standard thickness (mm)
t_1	15.52	17.02	18
t_2	13.8	15.3	16
t_3	12.04	13.54	14
t_4	10.3	11.8	12

t_5	8.56	10.06	10
t_6	6.82	8.32	8
t_7	5.08	6.58	7
t_8	3.34	4.84	6
t_9	1.6	3.1	6

CONCLUSION

We have covered various aspects at the completion this project "Production of Formaldehyde". After having done the literature survey, we systematically carried out material balances and energy balances along with designing two equipments which are used in the plant. Formaldehyde finds various uses in the commercial world today. The setting up of a formaldehyde plant in Assam is quite feasible as Assam has an abundance of natural gas from where methanol can be obtained.

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PROJECT REPORT ON

PRODUCTION OF NITRIC ACID

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8th SEMESTER

Under the guidance of
Prof. Tapan Jyoti Sarma

DEPARTMENT OF CHEMICAL ENGINEERING
ASSAM ENGINEERING COLLEGE

JALUKBARI, GUWAHATI- 781013
SESSION-2022-23

PRODUCTION OF NITRIC ACID

EIGHTH SEMESTER B.TECH PROJECT

Submitted in partial fulfillment of The Requirements of the Degree of

BACHELORS OF TECHNOLOGY

In
CHEMICAL ENGINEERING

Of

ASSAM SCIENCE AND TECHNOLOGY UNIVERSITY

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CERTIFICATE

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This is to certify that the project titled "**PRODUCTION OF NITRIC ACID**" submitted by the following students of 8th semester of Chemical Engineering Department.

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It is a bonafide work carried out by them required in partial fulfilment for the award of the degree of Bachelor of Technology in Chemical Engineering of Assam Science and Technology University, Guwahati, which may be accepted.

Date 30/6/2023

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ABSTRACT

The production of nitric acid is a crucial industrial process that plays a significant role in various sectors such as agriculture, pharmaceuticals, and explosives manufacturing. Nitric acid is a versatile chemical with a wide range of applications, including the production of fertilizers, dyes, plastics, and cleaning agents. This abstract provides an overview of the key aspects involved in the production of nitric acid.

The Dual Pressure Nitric Acid Process (DPNAP) is a widely employed method for the production of high-quality nitric acid. The primary method employed for nitric acid production is the Ostwald process, which involves the catalytic oxidation of ammonia to nitric oxide, followed by its subsequent oxidation to nitrogen dioxide and absorption in water to form nitric acid. The process is typically carried out in a multi-step sequence of reactions that require careful control of temperature, pressure, and concentration to ensure optimal conversion and yield.

The initial step in the Ostwald process involves the catalytic oxidation of ammonia over a platinum-rhodium catalyst, which produces nitric oxide (NO) and water vapor. This step is exothermic and requires a temperature range of approximately 800-900°C. The resulting nitric oxide is then oxidized further in the presence of excess air to form nitrogen dioxide ($NO2$), a highly reactive gas. This oxidation step occurs at a lower temperature range of 400-500°C and is facilitated by a catalyst such as platinum or vanadium pentoxide.

After the oxidation steps, the generated nitrogen dioxide is carefully mixed with water, leading to its absorption and subsequent reaction to form nitric acid ($HNO3$). The absorption process is highly exothermic and requires proper cooling and control of the reaction conditions to prevent the formation of undesirable by-products.

The final product, pure nitric acid, is stored in appropriate containers made of materials resistant to the corrosive nature of nitric acid, such as glass, high-density polyethylene (HDPE), or stainless steel. Safety precautions should be taken during storage and handling to prevent accidental spills or exposure to the acid.

It's important to note that the specific design and operating parameters of the dual pressure nitric acid process may vary depending on the scale of production; equipment used, and desired product specifications. The process also involves several safety considerations due to the corrosive and reactive nature of nitric acid, so appropriate safety measures must be implemented throughout the process.

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CHAPTER I
INTRODUCTION

1.1 BACKGROUND

NITRIC ACID

Nitric acid (*aqua fortis*) was known and its chemistry practiced in the middle Ages. It was obtained by heating hydrated copper sulphate or sulfuric acid with sodium nitrate (saltpetre or nitre) and cooling the vapours generated to obtain a solution of nitric acid .

$NaNO_3$“niter” +H_2SO_4→C$NaHSO_4$“nitercake” + HNO_3

While it is theoretically possible to obtain 2 moles of nitric acid for each mole of sulfuric acid used, 900°C temperature required makes this stoichiometry impractical. However, the residual acid value of the nitre cake could be used to make hydrochloric acid from salt.

$NaHSO_4$+NaCl→Na_2SO_4“saltcake” + HCl

In the 17th century, Johann Rudolf Glauber devised a process to obtain nitric acid by distilling potassium nitrate with sulfuric acid. In 1776 Antoine Lavoisier cited Joseph Priestley's work to point out that it can be converted from nitric oxide (which he calls "nitrous air"), "combined with an approximately equal volume of the purest part of common air, and with a considerable quantity of water."[40][a] In 1785 Henry Cavendish determined its precise composition and showed that it could be synthesized by passing a stream of electric sparks through moist air.[36] In 1806, Humphry Davy reported the results of extensive distilled water electrolysis experiments concluding that nitric acid was produced at the anode from dissolved atmospheric nitrogen gas. He used a high voltage battery and non-reactive electrodes and vessels such as gold electrode cones that doubled as vessels bridged by damp asbestos.[41]

The industrial production of nitric acid from atmospheric air began in 1905 with the Birkeland–Eyde process, also known as the arc process.[12] This process is based upon the oxidation of atmospheric nitrogen by atmospheric oxygen to nitric oxide with a very high temperature electric arc. Yields of up to approximately 4–5% nitric oxide was obtained at 3000°C, and less at lower temperatures.[4] The nitric oxide was cooled and oxidized by the remaining atmospheric oxygen to nitrogen dioxide, and this was subsequently absorbed in water in a series of packed column or plate column absorption towers to produce dilute nitric acid. The first towers bubbled the nitrogen dioxide through water and non-reactive quartz fragments. About 20% of the produced oxides of nitrogen remained unreacted so the final towers contained an alkali solution to neutralize the rest. The process was very energy intensive and was rapidly displaced by the Ostwald process once cheap ammonia became available.

Another early production method was invented by French engineer Albert Nodon around 1913. His method produced nitric acid from electrolysis of calcium nitrate converted by bacteria from nitrogenous matter in peat bogs. An earthenware pot surrounded by limestone was sunk into the peat and staked with tarred lumber to make a compartment for the carbon anode around which the nitric acid is formed. Nitric acid was pumped out from an earthenware [45] pipe that was sunk down to the bottom of the pot. Fresh water was pumped into the top through another earthenware pipe to replace the fluid removed. The interior was filled with coke. Cast iron cathodes were sunk into the peat surrounding it. Resistance was about 3 ohms per cubic meter and the power supplied was around 10 volts. Production from one deposit was 800 tons per year.[15][16] Once the Haber process for the efficient production of ammonia was introduced in 1913, nitric acid production from ammonia using the Ostwald process overtook production from the Birkeland–Eyde process. This method of production is still in use today.

For nitrogen fertilizers and for the nitric acid requirement for the manufacture of explosives in the 19th century, natural sodium (or potassium) nitrate provided the only source. India produced some 30,000 tonne/year by 1861 and Chile, in 1870, was exporting some 90,000 tonnes annually which gradually climbed to about 1.4 million tons/year, in both cases as sodium nitrate.

Present-day nitric acid production is almost entirely via the oxidation of ammonia and absorption of the oxidation products in water. The chemistry of this process was proven experimentally by Kuhlmann in 1839, but had to wait for the development of an economical route to ammonia before it could become commercially significant. Ostwald, working in Germany in about 1900, re-examine and extended Kuhlmann's data and established the proper conditions required for the ammonia oxidation step. Very shortly after these plants started operating on these principles were constructed both in Germany and the U.S. Since 1980, 3–5 million metric tonnes of nitric acid (100% basis) have been produced annually in Germany, and 7–9 million tonnes in the U.S[2]

In 1991, there were approximately 65 nitric acid (HNO_3) manufacturing plants in the U. S. with a 3 total capacity of 11 million tons of HNO per year. The plants range in size from 6,000 to 700,000 tons per 3 years. About 70 percent of the nitric acid produced is consumed as an intermediate in the manufacture of ammonium nitrate (NH NO), which in turn is used in fertilizers. The majority of the nitric acid plants are located in agricultural regions such as the Midwest, South Central, and Gulf States because of the high demand for fertilizer in these areas. Another 5 to 10 percent of the nitric acid produced is used for organic oxidation in adipic acid manufacturing. Nitric acid is also used in organic oxidation to manufacture terephthalic acid and other organic compounds. Explosive manufacturing utilizes nitric acid for organic nitration. Nitric acid nitration is used in producing nitrobenzene, nitrotoluenes, and other chemical intermediates. Other end uses of nitric acid are gold and silver separation, military munitions, steel and 1 brass pickling, photoengraving, and acidulation of phosphate rock. [1]

1.2 PHYSICAL AND CHEMICAL PROPERTIES

1.2.1 Contamination with Nitrogen dioxide

Nitric acid is subject to thermal or light decomposition and for this reason it was often stored in brown glass bottles:

$$4HNO_3 \rightarrow 2\,H_2O + 4\,NO_2 + O_2$$

This reaction may give rise to some non-negligible variations in the vapor pressure above the liquid because the nitrogen oxides produced dissolve partly or completely in the acid.

The nitrogen dioxide (NO_2) and/or dinitrogen tetroxide (N_2O_4) remains dissolved in the nitric acid colouring it yellow or even red at higher temperatures. While the pure acid tends to give off white fumes when exposed to air, acid with dissolved nitrogen dioxide gives off reddish-brown vapours, leading to the common names "red fuming nitric acid" and "white fuming nitric acid". Nitrogen oxides (NO_x) are soluble in nitric acid.

1.2.2 Fuming Nitric acid

Commercial-grade fuming nitric acid contains 98% HNO_3 and has a density of 1.50 g/cm^3. This grade is often used in the explosives industry. It is not as volatile nor as corrosive as the anhydrous acid and has the approximate concentration of 21.4 M.

Red fuming nitric acid, or RFNA, contains substantial quantities of dissolved nitrogen dioxide (NO_2) leaving the solution with a reddish-brown colour. Due to the dissolved nitrogen dioxide, the density of red fuming nitric acid is lower at 1.490 g/cm^3.

1.2.3 Anhydrous Nitric acid

White fuming nitric acid, pure nitric acid or WFNA, is very close to anhydrous nitric acid. It is available as 99.9% nitric acid by assay. One specification for white fuming nitric acid is that it has a maximum of 2% water and a maximum of 0.5% dissolved NO_2. Anhydrous nitric acid has a density of 1.513 g/cm^3 and has the approximate concentration of 24 molar. Anhydrous nitric acid is a colourless mobile liquid with a density of 1.512 g/cm^3 that solidifies at −42 °C (−44 °F) to form white crystal. As it decomposes to NO_2 and water, it obtains a yellow tint. It boils at 83 °C (181 °F). It is usually stored in a glass shatterproof amber bottle with twice the volume of head space to allow for pressure build up, but even with those precautions the bottle must be vented monthly to release pressure

Table 1: Properties of Nitric acid

PROPERTIES	
Chemical formula	HNO_3
Molar mass	63.012 g·mol^{-1}
Appearance	Colourless liquid
Odor	Acid, suffocating
Density	1.51 g/cm^3, 1.41 g/cm^3 [68% w/w]
Melting point	−42 °C (−44 °F; 231 K)

Boiling point	83 °C (181 °F; 356 K) 68% solution boils at 121 °C (250 °F; 394 K)
Solubility in water	Miscible
log *P*	−0.13
Vapor pressure	48 mmHg (20 °C)
Acidity (pK_a)	−1.4
Conjugate base	Nitrate
Magnetic susceptibility (χ)	-1.99×10^{-5} cm^3/mol
Refractive index (n_D)	1.397 (16.5 °C)
Dipole moment	2.17 ± 0.02

1.2.4 Reaction with Nitric Acid

- **Acid-base properties**

Nitric acid is normally considered to be a strong acid at ambient temperatures. There is some disagreement over the value of the acid dissociation constant, though the pK_a value is usually reported as less than −1. This means that the nitric acid in diluted solution is fully dissociated except in extremely acidic solutions. The pK_a value rises to 1 at a temperature of 250 °C. [3]

Nitric acid can act as a base with respect to an acid such as sulfuric acid:

$$HNO_3 + 2\ H_2SO_4 \rightleftharpoons [NO_2]^+ + [H_3O]^+ + 2\ HSO\text{–}4;\ \text{Equilibrium constant: } K \approx 22$$

The nitronium ion, $[NO_2]^+$, is the active reagent in aromatic nitration reactions. Since nitric acid has both acidic and basic properties, it can undergo an autoprotolysis reaction, similar to the self-ionization of water:

$$2HNO_3 \rightleftharpoons [NO_2]^+ + NO^{-3} + H_2O$$

- **Reactions with metals**

Nitric acid reacts with most metals, but the details depend on the concentration of the acid and the nature of the metal. Dilute nitric acid behaves as a typical acid in its reaction with most metals. Magnesium, manganese, and zinc liberate H_2:

$$Mg + 2\ HNO_3 \rightarrow Mg(NO_3)_2 + H_2 \text{ ------- } (1)$$
$$Mn + 2\ HNO_3 \rightarrow Mn(NO_3)_2 + H_2 \text{ --------}(2)$$

$Zn + 2\ HNO_3 \rightarrow Zn(NO_3)_2 + H_2$----------(3)

Nitric acid can oxidize non-active metals such as copper and silver. With these non-active or less electropositive metals the products depend on temperature and the acid concentration. For example, copper reacts with dilute nitric acid at ambient temperatures with a 3:8 stoichiometry:

$$3\ Cu + 8\ HNO_3 \rightarrow 3\ Cu(NO_3)_2 + 2\ NO + 4\ H_2O$$

The nitric oxide produced may react with atmospheric oxygen to give nitrogen dioxide. With more concentrated nitric acid, nitrogen dioxide is produced directly in a reaction with 1:4 stoichiometry:

$$Cu + 4\ H^+ + 2\ NO{-}3 \rightarrow Cu^{2+} + 2\ NO_2 + 2\ H_2O$$

Upon reaction with nitric acid, most metals give the corresponding nitrates. Some metalloids and metals give the oxides; for instance, Sn, As, Sb, and Ti are oxidized into SnO_2, As_2O_5, Sb_2O_5, and TiO_2 respectively.[3]

Some precious metals, such as pure gold and platinum-group metals do not react with nitric acid, though pure gold does react with *aqua regia*, a mixture of concentrated nitric acid and hydrochloric acid. However, some less noble metals (Ag, Cu, ...) present in some gold alloys relatively poor in gold such as colored gold can be easily oxidized and dissolved by nitric acid, leading to colour changes of the gold-alloy surface. Nitric acid is used as a cheap means in jewellery shops to quickly spot low-gold alloys (< 14 karats) and to rapidly assess the gold purity.

- **Reactions with non-metals**

Being a powerful oxidizing acid, nitric acid reacts with many organic materials, and the reactions may be explosive. The hydroxyl group will typically strip a hydrogen from the organic molecule to form water, and the remaining nitro group takes the hydrogen's place. Nitration of organic compounds with nitric acid is the primary method of synthesis of many common explosives, such as nitro-glycerine and trinitrotoluene (TNT). As very many fewer stable byproducts are possible, these reactions must be carefully thermally controlled, and the byproducts removed to isolate the desired product.

Reaction with non-metallic elements, with the exceptions of nitrogen, oxygen, noble gases, silicon, and halogens other than iodine, usually oxidizes them to their highest oxidation states as acids with the formation of nitrogen dioxide for concentrated acid and nitric oxide for dilute acid.

$C\ (graphite) + 4\ HNO_3 \rightarrow CO_2 + 4\ NO_2 + 2\ H_2O$ ---------(1)

$3C\ (graphite) + 4\ HNO_3 \rightarrow 3\ CO_2 + 4\ NO + 2\ H_2O$ --------(2)

Concentrated nitric acid oxidizes I_2, P_4, and S_8 into HIO_3, H_3PO_4, and H_2SO_4, respectively.[13] Although it reacts with graphite and amorphous carbon, it does not react with diamond; it can separate diamond from the graphite that it oxidizes.[4]

- **Xanthoproteic test**

Nitric acid reacts with proteins to form yellow nitrated products. This reaction is known as the xanthoproteic reaction. This test is carried out by adding concentrated nitric acid to the substance being tested, and then heating the mixture. If proteins that contain amino acids with aromatic rings are present, the mixture turns yellow. Upon adding a base such as ammonia, the colour turns orange. These colour changes are caused by nitrated aromatic rings in the protein.[15][16] Xanthoproteic acid is formed when the acid contacts epithelial cells. Respective local skin colour changes are indicative of inadequate safety precautions when handling nitric acid.

1.3 USES AND APPLICATIONS OF NITRIC ACID

The main industrial use of nitric acid is for the production of fertilizers. Nitric acid is neutralized with ammonia to give ammonium nitrate. This application consumes 75–80% of the 26 million tonnes produced annually (1987). The other main applications are for the production of explosives, nylon precursors, and specialty organic compounds.[11]

- **Precursor to organic nitrogen compounds**

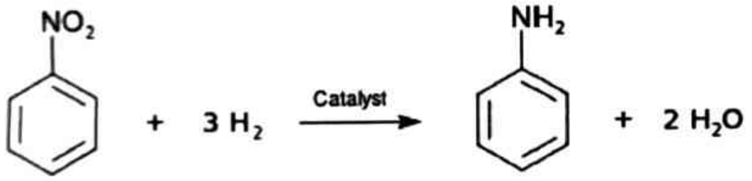
In organic synthesis, industrial and otherwise, the nitro group is a versatile functional group. A mixture of nitric and sulfuric acids introduces a nitro substituent onto various aromatic compounds by electrophilic aromatic substitution. Many explosives, such as TNT, are prepared this way:

$C_6H_5CH_3 + 3\ HNO_3 \rightarrow C_6H_2(NO_2)_3CH_3 + 3\ H_2O$ -------(1)

Either concentrated sulfuric acid or oleum absorbs the excess water.

$H_2S_2O_7 + H_2O \rightarrow 2\ H_2SO_4$ ---------(2)

The nitro group can be reduced to give an amine group, allowing synthesis of aniline compounds from various nitro-benzenes:



-----------(3)

- **Use as an oxidant**

The precursor to nylon, adipic acid, is produced on a large scale by oxidation of "KA oil"—a mixture of cyclohexanone and cyclohexanol—with nitric acid.[21]

- **Rocket propellant**

Nitric acid has been used in various forms as the oxidizer in liquid-fuelled rockets. These forms include red fuming nitric acid, white fuming nitric acid, mixtures with sulfuric acid, and these forms with HF inhibitor.[22] IRFNA (inhibited red fuming nitric acid) was one of three liquid fuel components for the BOMARC missile.[23]

- **Metal processing**

Nitric acid can be used to convert metals to oxidized forms, such as converting copper metal to cupric nitrate. It can also be used in combination with hydrochloric acid as aqua regia to dissolve noble metals such as gold (as chloroauric acid). These salts can be used to purify gold and other metals beyond 99.9% purity by processes of recrystallization and selective precipitation. Its ability to dissolve certain metals selectively or be a solvent for many metal salts makes it useful in gold parting processes.

- **Analytical reagent**

In elemental analysis by ICP-MS, ICP-AES, GFAA, and Flame AA, dilute nitric acid (0.5–5.0%) is used as a matrix compound for determining metal traces in solutions.[14] Ultrapure trace metal grade acid is required for such determination, because small amounts of metal ions could affect the result of the analysis.

It is also typically used in the digestion process of turbid water samples, sludge samples, solid samples as well as other types of unique samples which require elemental analysis via ICP-MS, ICP-OES, ICP-AES, GFAA and flame atomic absorption spectroscopy. Typically, these digestions use a 50% solution of the purchased HNO_3 mixed with Type 1 DI Water.

In electrochemistry, nitric acid is used as a chemical doping agent for organic semiconductors, and in purification processes for raw carbon nanotubes.

- **Woodworking**

In a low concentration (approximately 10%), nitric acid is often used to artificially age pine and maple. The colour produced is a grey-gold very much like very old wax- or oil-finished wood (wood finishing).[25]

- **Etchant and cleaning agent**

The corrosive effects of nitric acid are exploited for some specialty applications, such as etching in printmaking, pickling stainless steel or cleaning silicon wafers in electronics.[26]

A solution of nitric acid, water and alcohol, nital, is used for etching metals to reveal the microstructure. ISO 14104 is one of the standards detailing this well-known procedure. Nitric acid is used either in combination with hydrochloric acid or alone to clean glass cover slips and glass slides for high-end microscopy applications.[27] It is also used to clean glass before silvering when making silver mirrors.[28]

Commercially available aqueous blends of 5–30% nitric acid and 15–40% phosphoric acid is commonly used for cleaning food and dairy equipment primarily to remove precipitated calcium and magnesium compounds (either deposited from the process stream or resulting from the use of hard water during production and cleaning). Nitric acid can be used as a spot test for alkaloids like LSD, giving a variety of colours depending on the alkaloid.[29]

- **Nuclear fuel reprocessing**

Nitric acid plays a key role in PUREX and other nuclear fuel reprocessing methods, where it can dissolve many different actinides. The resulting nitrates are converted to various complexes that can be reacted and extracted selectively in order to separate the metals from each other.

CHAPTER 2

LITERATURE REVIEW

2.1) In the study conducted by V.A. Sadykov et.al.[17] dicusses about the role of oxide catalyst in the nitric acid production. They studied about the factors that affect the performances of precious metals and the oxides during high temperature in ammonia oxidation process. They also analysed the synthesis of mixed oxide systems which also includes the perovskites that control the nitric acid selectivity and stability in high temperature during the ammonia oxidation process.

2.2) In the study conducted by T.et.al.[15] which discusses about the manufacturing of nitric acids by the ammonia oxidation process and the production of concentrated acid by considering the air pollution aspects of the process.

2.3) In the study conducted by Uhde GmbH's et al.[16] discusses about the Dual Pressure Process uses the Ostwald Process for Ammonia Oxidation as a starting point of Nitric Acid production and NO gas absorption to concentrate the nitric acid formed while cooling of the reaction gases.

2.4) In the study conducted Richard W. Gerstle et.al[3]. discusses about the typical nitric acid concentration unit. 60 percent nitric acid to the top of a packed dehydrating column where it flows downward countercurrent to ascending vapors. Concentrated nitric leaves the top of the column as 98 percent vapor containing a small amount of NOR and 02 resulting from dissociation of nitric acid.

2.5) In the study conducted B. J. Adelman et.al[2]. discusses about the catalysts like radium pentoxide, platinum, iron, chromium oxide and zeolites are commonly used during the reaction Catalyst efficiency and gas temperature are the two factors on which the leakage through the catalyst bed depends upon. Temperature during the operation is generally kept more than 200OC whereas, efficiency of ammonia is minimally affected by the pressure.

2.6)In the study conducted by Ata ul Rauf Salman S. M.et.al. [2] discusses about the NO oxidation is a key response in lean NOx reduction advancements and in the Ostwald cycle for nitric acid creation. In Ostwald's cycle, NO oxidation is completed as a non-catalytic measure and the forward response is supported by the evacuation of heat and by giving adequate habitation time. Utilizing a catalyst for NO oxidation may prompt intensification of the nitric acid plant. Along with accelerating the oxidation cycle, it might decrease capital expenses and increment heat recovery.

2.7) In the study conducted by Dr.-Carl von Linde.et.al.[5] discusses about the medium pressure nitric acid. current production route of nitric acid is known as "the Ostwald process" and has been used for nearly a century. In this process, ammonia is combusted (oxidized) in air, to nitricoxide (NO). This highly exothermic reaction is carried out over a highly selective platinum–rhodium catalyst. The temperature ranges between 800 and 930 °C.

2.8) In the study conducted by Dr.-Carl von Linde.et.al. [7] discusses about the NO_2 absorption in water to form nitric acid. The absorption of a gas by a fluid is a fundamental designing unit operation which has been very much examined. At the point when it is desired to structure an item, as on account of nitrogen dioxide absorption by water to frame nitric acid, or to clean an emanating gas stream.

2.9)In the study conducted by J R Ferrer and L M Marzo[6] on the highlights in production costs of dual pressure process for nitric acid manufacture, the dual process for nitric acid production has clear advantage over the mono pressure process, especially for large plants. Amore sound comparison of the unit consumptions should be made over measurements made over a complete year.

2.10)In the study conducted by Gorica R Ivanis et. al,[7] pinch methodology was applied to HEN of nitric acid production and results are presented in two ways based on original heat transfer equipment and optimization of the previous parameters.

CHAPTER 3
PRODUCTION OF NITRIC ACID

3.1 PROCESS ROUTES FOR PRODUCTION OF NITRIC ACID

- ### CHILE SALTPETRE/NITRATE PROCESS

Chile saltpetre is material which contains sodium nitrate NaNO, with percentage around 35-60%, and remaining percentage compounds with KNO, and NaCl. This raw material Chile saltpetre is concentrated by crystallization in pre-treatment of ore to attain 95% $NaNO_3$, and remaining KNO, as feed raw material. (Kent 1983). Sulphuric acid with 93% is mixed with the refined Chile saltpetre as per the ratio required as per stoichiometry and sent into a retort which is made with cast iron and the mixture is heated to 200°C with help of furnace flue gasses and coal fire. Thus at this temperature, the following reaction is carried forward to produce HNO_3, nitric acid vapors.

$NaNO_3+H_2SO_4 \rightleftharpoons NaHSO_4, + HNO_3$

All hot vapors of nitric acid are sent to cool down in water circulated cooled silica pipes. Condensed HNO_3 are collected in receiver which has material resistance to nitric acid. Uncondensed gas which escapes from the collector is scrubbed with cooled water in packed bed tower to collect nitric acid in dilute format. Liquid sodium bi-sulphate is collected from the bottom outlet of the retort.

Advantage: it was one of the first methods used in the manufacture of nitric acid.

Disadvantage: Source of raw material can be exhausted.

- ### BIRKELAND-EYDE PROCESS/ARC PROCESS

This process is based upon the oxidation of atmospheric nitrogen by atmospheric oxygen to nitric oxide at very high temperature. An electric arc is used to provide the high temperatures, and yields of up to 4% nitric oxide were obtained. (Ohrue1999).

$N_2+O_2 \rightarrow 2NO$ ------(1)

The nitric oxide was cooled and oxidized by the remaining atmospheric oxygen to nitrogen dioxide.

$2\,NO+O_2 \rightarrow 2NO_2$ ------- (2)

This nitrogen dioxide is then dissolved in water to give dilute nitric acid.

$3\,NO_2 + H_2O \rightarrow 2HNO_3+NO$ ----------(3)

Advantage: unlimited source of raw material (air).

Disadvantage: The process is very energy intensive and is only feasible when electricity is available and cheap.

• OSTWALD PROCESS

In this process, anhydrous ammonia is oxidized to nitric oxide, in the presence of platinum or rhodium gauge catalyst at high temperature of about 500K and a pressure of 9bar. (Ray et al 1989)

$4\ NH_3+50_2 \longrightarrow 4\ NO + 6\ H2O$ (ΔH - -905.2 KJ/mol) -------(1)

Nitric acid is then reacted with oxygen in air to form nitrogen dioxide.

$2\ NO+O_2 \longrightarrow NO$ --------(2) (ΔH- -114KJ/mol) -------(2)

This is subsequently absorbed in water to form nitric acid and nitric oxide

$3\ NO+H2O \longrightarrow HNO + NO$ (ΔH-117KJ/mol) -------(3)

The nitric oxide is cycled back for re-oxidation. Alternately, if the last step is carried out in air, then :

$4\ NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$ ------- (4)

The aqueous HNO_3, obtained can be concentrated by distillation up to about 68% by mass There are 2 basic types of systems used to produce weak nitric acid. Both processes follow the basic Ostwald process for the catalytic oxidation of ammonia. In summary, this involves an oxidation stage whereby ammonia is reacted with air in a catalytic converter at temperatures in the range of 850-950°C. Reaction gases pass through a series of energy recovery stages before entering an absorption column. The bottoms from the column are bleached of dissolved nitrogen peroxide using air, and the resulting solution is the weak nitric acid product (Roudier et al 1979).

The major difference between the two processes lies in the initial conversion stage. The dual-pressure process employs a conversion stage operating in the range 100-350kPa, and a reactor temperature of about 865°C. The single-pressure process however operates the converter at 800-1100 kPa, with a reactor temperature closer to 940^0C. (Harvin et al 1979)

1. Single-stage pressure process in this case, the plant is operated at a single pressure throughout.

Advantage:

i) Less expensive as less equipment's are used.
ii) The single-pressure process uses a higher ammonia conversion pressure. This higher pressure provides advantages in terms of equipment design, e.g. smaller converter dimensions and a single heat-exchanger-train layout. (Leray et al 1979) The higher temperature and the favourable pressure both increase the energy recovery from the process.
iii) Limited space availability may favour the single-pressure process+

Disadvantage:

i) Less efficient as the overall process is favoured by varying pressure.

ii) Experimental work indicates that the rate loss of catalyst (without a catalyst recovery system) is approximately three times more rapid at 973 C than at 866°C. This means that more catalyst is lost in the single-stage pressure process (Harvin et al 1979).

iii) Absorber efficiency is reduced prompting the need for larger absorber thereby increasing cost.

TABLE 2: COMPARISON OF DIFFERENT PROCESSES OF NITRIC ACID PRODUCTION

PROCESS NUMBER	**1**	**2**	**3**	**4**
NAME OF THE PROCESS	OSTWALD PROCESS (ammonia oxidation)	BIRKELAND–EYDE PROCESS	CHILE SALTPETER PROCESS	DUAL /SINGLE PRESSURE PROCESS
RAW MATERIAL	AMMONIA, AIR, WATER	AIR, WATER	SODIUM NITRATE, SULPHURIC ACID	AMMONIA, AIR, WATER
REACTION	Oxidation of NH_3 to NO Oxidation of NO to NO_2 Absorption of NO_2 in water Concentration of HNO_3,	Electrical arcs react with atmospheric N_2 with oxygen (O_2) to produce HNO_3	Sulphuric acid is mixed with the refined Chile saltpetre as per the and sent into a retort which is made with cast iron and the mixture is heated to 200°C with help of furnace flue gasses and coal fire	Oxidation of NH_3 to NO Oxidation of NO to NO_2 Absorption of NO_2 in water Concentration of HNO_3,
BY PRODUCT	Steam	Water	$NaHSO_4$	NO, NO_2, off gases
CONVERSION%	57-60%	40–50%	50%	96 %
YIELD%	93-96%	96%	-	96%
CATALYST	Pt (90%)-Rh (10%) Alloy	-	-	Pt (90%)-Rh (10%) Alloy
OPERATING TEMPERATURE	870–1,073 K	Arc temperature of 3000K	200-300K	870–1,073 K

OPERATING PRESSURE	4–10 standard atmospheres (410–1,000 kPa; 59–150 psi)	Atmospheric pressure	Atmospheric pressure	4–10 standard atmospheres (410–1,000 kPa; 59–150 psi)
ADVANTAGE	. Acid quality and yield is improved capital requirement is 10% operating cost half to Chile Salt-Peter process	Availability of raw material that is air	Easier process	. Acid quality and yield is improved capital requirement is 10% operating cost half to Chile Salt-Peter process
DISADVANTAGE	Cost Of The Catalyst Is High	Energy intensive process hydroelectric power station for the electricity, alternating current of 5 kV at 50 Hz.	Availability of raw material is scarce.	Cost Of The Catalyst Is High

3.2 FINAL PROCESS SELECTION

Most nitric acid processes are design with the absorption section operating under high pressure. In the contemporary climate of high energy and metal costs, the dual pressure process for the nitric acid manufacture has clear economy advantage over the mono pressure process especially for large plants. Efficiency of ammonia decreases with time. The yield of the dual-pressure method begins at close to 97% and subsequently declines to about 95% after six months. The mono high-pressure method, in comparison, begins with an initial yield of around 94%, but after just about three months of operation, it soon drops to about 90%. The net consumption of precious metal catalyst per tonne of 100% nitric acid is 35 mg in a dual-pressure plant and as high as 90 mg in a mono high-pressure plant. In the current climate of high energy and metal cost, the economics of the dual pressure process are superior to those of the mono high-pressure process by a clear margin, at least in large capacity plants.

A dual-pressure process permits:

- exploiting the cooling effect of evaporating ammonia at low pressure to operate the absorption at low temperature, minimising residual NOx in the tail gas;
- oxidizing the ammonia in optimum yield conditions with minimum losses of catalyst;
- Higher concentration in final product (68%);
- lower NO_2 content in final product

Against this must be set the slightly higher investment cost resulting from need for a nitrous gas compressor and low-pressure heat exchangers. Therefore, we have opted for the dual pressure process for the nitric acid production

3.3 DUAL PRESSURE PROCESS FOR NITRIC ACID PRODUCTION

PROCESS DESCRIPTION

- Air is pumped into the plant at ambient conditions (1 bar, 25°C), entirely by the suction force provided by the centrifugal compressor. Air is then fed to the compressor. The compressor is used to increase the pressure of the air feed to 5 bars, also causing an increase in the temperature to 240-250°C. Liquid Ammonia from storage is pumped into the plant at -15°C and 12 bars, into Evaporator by a Centrifugal Pump. In the Evaporator, Ammonia is converted to vapor and further superheated to 70°C with the help of LP Steam (4-5 bar, 150°C) in the upper section of the Evaporator.

- The superheated ammonia vapor and the compressed air stream are mixed in a static mixer, coming out at 5 bar, 220-230°C. It is ensured that Ammonia to Air ratio is kept 1:9 by weight. The mixer outlet stream is fed into the reactor, which is a shallow bed reactor, with around 8-10 catalyst gauzes, made up of 90%Pt and 10%Rh. The catalyst is highly selective, giving a conversion of 96% for Ammonia into Nitric Oxide, gas stream exiting at a temperature of 890°C, consisting mainly of Nitrogen and Oxygen from Air feed and Nitric Oxide formed via Ammonia oxidation. Couple of side reactions also take place in the reactor with a total conversion of 4% for Ammonia.

- The high heat of reaction is used to make steam and heat other streams throughout the plant. A Shell and Tube Heat Exchanger is used to heat the tail gas coming from Absorption Column to facilitate the abatement process and another Shell and Tube Heat Exchanger is used as an economiser, which results in the temperature of the stream to drop to 185°C.

- Condenser 1 (Low pressure condenser), is used to cool the stream further, condense water and nitric acid and separate them out for further processing. The temperature of the outlet streams is around 45°C. This drop in temperature allows Nitric Oxide to oxidise to Nitrogen Dioxide at a much higher conversion rate when compared to the previous two heat exchangers.

- Nitrogen Dioxide is produced, with the drop in temperature and elevated pressure, some of it gets absorbed into the condensed Water formed in the reactor. Once absorbed, Nitrogen Dioxide combines with Water to form Nitric Acid and Nitric Oxide, which further gets oxidised to Nitrogen Dioxide, which again forms Nitric acid and so on.

- The Nitric Acid solution in the condensate of the Condenser-1, is then pumped to the Absorption Column to increase the Nitric Acid concentration in the solution. Compressor outlet is the fed to Condenser-2 (high pressure condenser), where process similar to that in Cooler Condenser-1 occurs, providing us with more weak Nitric Acid condensate.

- The vapor outlet of the condenser-1, mainly consisting of NOx gases, is passed through the NOx Compressor, elevating the pressure of the stream to 12 bars and the temperature to around 165°C. Compressor outlet is the fed to Condenser-2, where process similar to that in Condenser-1 occurs, providing us with weaker Nitric Acid condensate, which is pumped to the Absorption Column. Stream cooled after the second compressor is also fed to Absorption Column. The Absorption Column NOx gases fed at the bottom-most stage, process water fed at the top-most stage, acid condensate from the Cooler Condensers fed to an intermediate stage and cooling water coils at every stage throughout the column to maintain the column at a reduced temperature.

- Inside the column, Nitric Oxide oxidation to Nitrogen Dioxide occurs between stages in the vapor phase, and absorption of Nitrogen Dioxide into water and the formation of Nitric Acid from the absorbed Nitrogen Dioxide occur in the liquid phase on the sieve trays of the column. Bottom outlet of the column is called Red Fuming Nitric Acid, due to the red colour imparted by the dissolved Nitrogen Dioxide, giving us the final product acid with a 68% wt% solution.

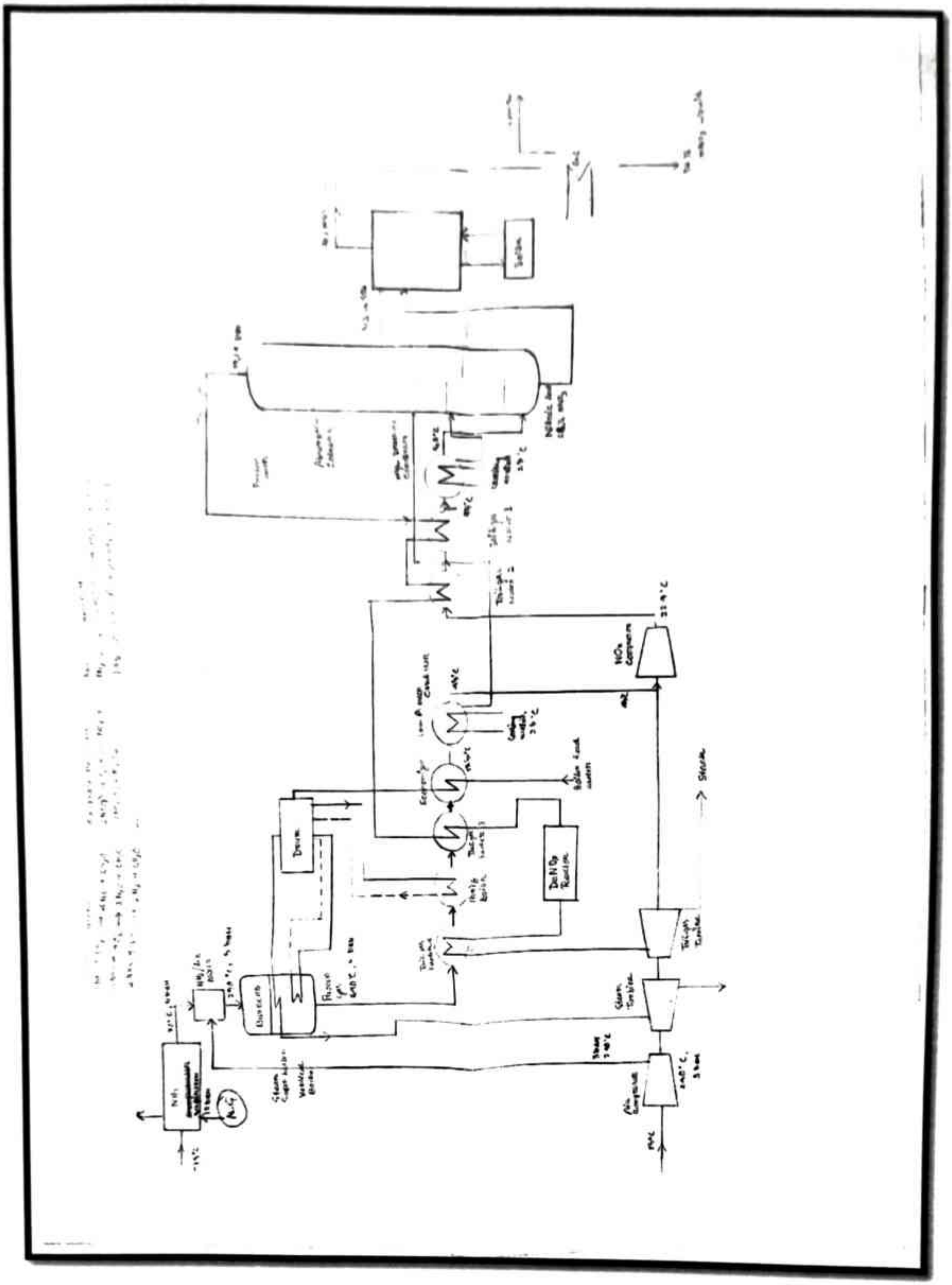


FIG.1 PROCESS FLOW DIAGRAM OF NITRIC ACID PRODUCTION THROUGH DUAL PRESSSURE PROCESS

HIGH STRENGTH NITRIC ACID PRODUCTION:

- A high strength nitric acid (96-98% concentration) can be obtained by concentrating the weak nitric acid using extractive distillation carried out in the presence of a dehydrating agent such as Concentrated Sulphuric acid.

- The process begins with the Concentrated Sulphuric acid being fed to the top of a dehydrating tower at atmospheric pressure. The acid mixture flows downwards counter-current to the ascending vapors.

- Concentrated Nitric acid (96-98%) leaves the column from the top and is further sent to a condenser for condensation into liquid. Emissions from this process are relatively minor, and a small absorber can be used to recover NO_2.

CHAPTER 4

MATERIAL BALANCE

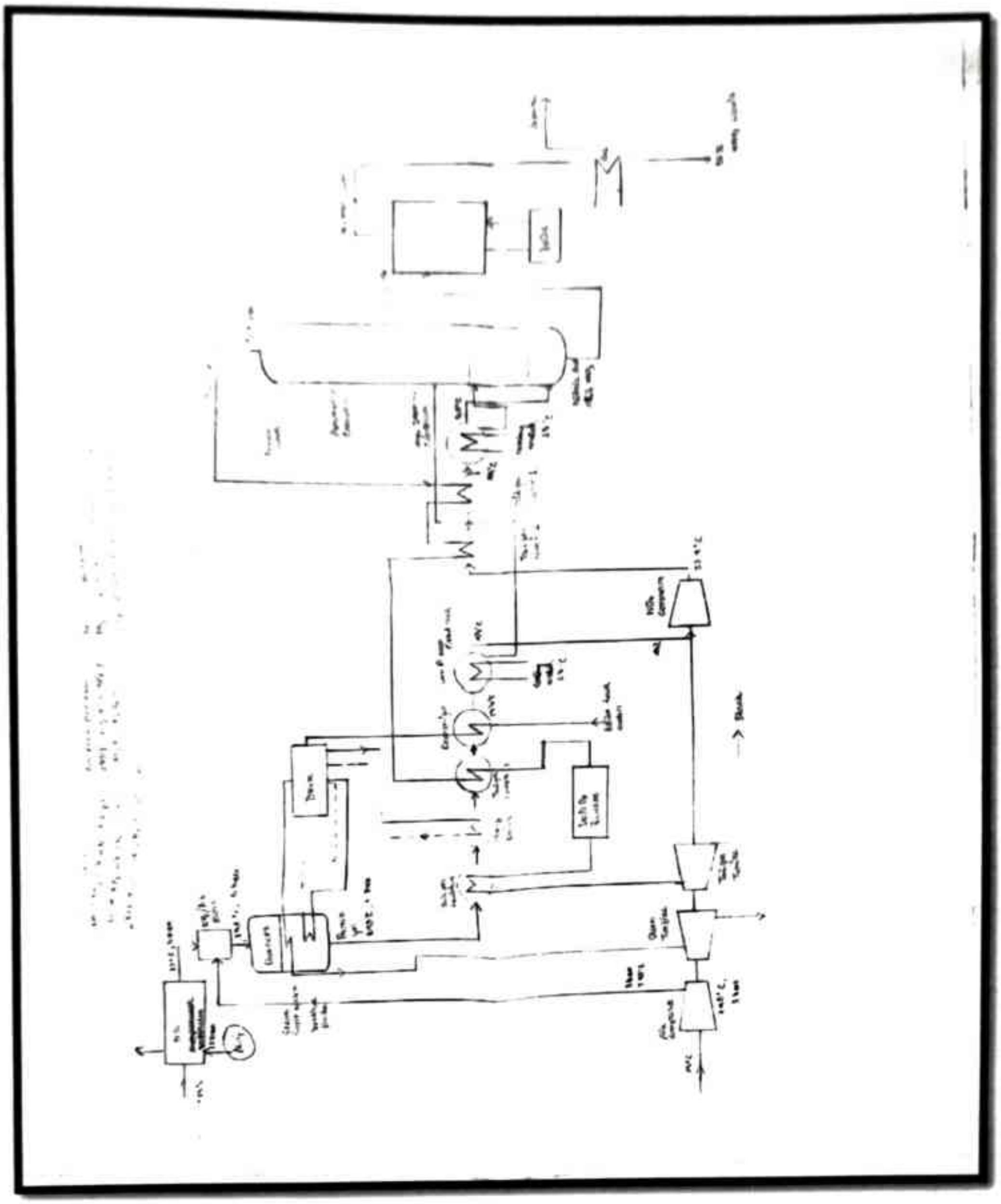


FIG 1. PROCESS FLOW DIAGRAM OF NITRIC ACID PRODUCTION THROUGH DUAL PRESSSURE PROCESS

1. MATERIAL BALANCE OVER MIXER AND BURNER

FIG 1.1

NO, Unreacted oxygen, water, Dinitrogen oxide

BASIS:

100 kmol of Ammonia

99.9% pure Ammonia as feedstock

Rest 0.1% - 0.079 % Nitrogen

- 0.021 % Oxygen

96 % yield of Nitrogen oxide

4% conversion in side reaction

1: 9 w/w Ammonia : Air mixture

(1) $4NH_3+ 5O_2 \longrightarrow 4NO + 6H_2O$ (96% CONVERSION)

NH_3 reacted= 95.940 kmol

O_2 reacted=119.88 kmol

NO produced=95.904 kmol

H_2O produced=143.856 kmol

(2) $4NH_3+ 3O_2 \longrightarrow 2N_2 + 6H_2O$(2%conversion)

NH_3 reacted= 1.998 kmol

O_2 reacted=1.998 kmol

N_2O produced=0.999 kmol

H_2O produced=2.997kmol

(3) $4NH_3+ 4O_2 \longrightarrow 2N_2O + 6H_2O$(2%conversion)

NH_3 reacted= 1.998 kmol

O_2 reacted=1.4985 kmol

N_2O produced=0.999 kmol

H_2O produced=2.997kmol

Total O_2 reacted =1.998+1.4985+119.88=123.3765 kmol

Total N_2 =0.999 kmol

Total N_2O=0.999 kmol

Total H_2O= 149.85 kmol

Air supplied =900 kmol

O_2 in air = 189 kmol

Total O_2 in air = 189 kmol

N_2 in air=711 kmol

Total N_2 in air=711.079 kmol

O_2 unreacted= 65.6445kmol

N_2 in outlet=712.078 kmol

	INLET		**OUTLET**	
	Kmol	**kg**	**kmol**	**kg**
NH_3	100	1700	--	--
O_2	189.021	6048.672	65.6445	2100.624
N_2	711.079	19910.212	712.078	19938.184
H_2O	-	-	149.85	2697.3
NO	-	-	95.904	2877.12
N_2O	-	-	0.999	43.956
TOTAL		27658.8		27658.8

TABLE 4.1 MATERIAL BALANCE ON MIXER AND BURNER

2. TAIL GAS HEATER 4, HORIZONTAL BOILER, TAIL GAS HEATER 3

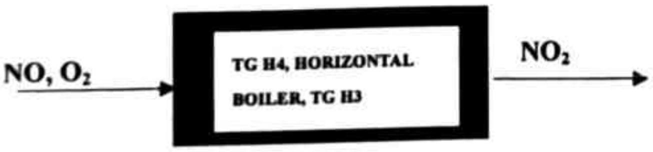


FIG 1.2

$2NO + O_2 \longrightarrow 2NO_2$ (Conversion- 40%)

NO reacted = 38.3616 kmol
O_2 reacted = 19.1808 kmol
NO_2 produced = 38.3616kmol

	INLET		**OUTLET**	
Component	**kmol**	**kg**	**kmol**	**kg**
NO	38.3616	1150.848	-	-
O_2	19.1808	613.7856	-	-
NO_2	-	-	38.3616	1764.6336
TOTAL		1764.6336		1764.6336

TABLE 4.2 : MATERIAL BALANCE ON A SERIESS OF HEAT EXCHANGERS

3. LP COOLER CONDENSER

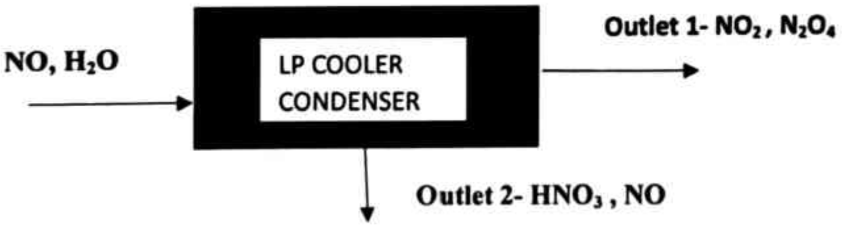


FIG 1.3

GAS PHASE REACTION (Total conversion =20%)

3.a)$2NO + O_2 \rightleftarrows 2NO_2$ – (1) (Conversion to NO_2 - 50%)

NO reacted=28.7712kmol

O2 reacted =14.3856 kmol
NO2 formed =28.7712 kmol

3.b)$2NO_2 \rightleftharpoons N_2O_4$ – (2) (Conversion to N_2O_4 - 30%)

NO_2 reacted = 8.6336 kmol

N_2O_4 formed=40.31568kmol

LIQUID PHASE REACTION (Total conversion to nitric acid – 20 %)
30%w/w HNO_3 formed

3.c) $3NO_4 + 2H_2O \rightleftharpoons 4HNO_3 + 2NO$ - (3) (10%conversion)

N_2O_4 reacted=0.431568 kmol
H_2O required=0.287712 kmol
HNO_3 formed=0.575424 kmol
NO formed=0.287712 kmol

3.d) 3NO2 + H2O $\rightleftharpoons$ 2HNO3 + NO - (4) (10%conversion)

NO_2 Reacted =0.2013984kmol
H_2O Reacted= 0.0671328 kmol
HNO_3 Formed=0.1342656 kmol
NO Formed= 0.0671328kmol

H2O Unreacted=149.4951552kmol
=2690.912794kg
O_2 Unreacted=32.0781kmol
=1026.4992kg

	INLET		OUTLET(1+2)	
Component	**Kmol**	**kg**	**kmol**	**kg**
O_2	46.4637	1486.8384	32.0781	1026.4992
H_2O	149.85	2697.3	149.4951552	2690.912794
NO	28.7712	863.136	0.3548448	10.645344
N_2O_4	-	-	3.884112	357.338304
NO_2	-	917.1683136	19.9384416	917.1683136

TABLE 4.3 : MATERIAL BALANCE OVER CONDENSER 1

4. NOx COMPRESSOR

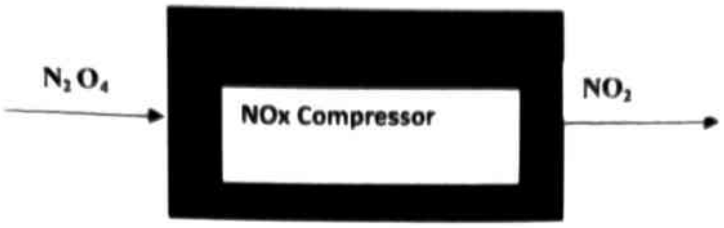


FIG1.4

$2N_2O_4 \rightleftharpoons 2NO_2$ **(Conversion- 80%)**

	INLET		**OUTLET**	
Component	**kmol**	**kg**	**kmol**	**kg**
N_2O_4	3.1072896	285.8706432	-	-
NO_2	-	-	6.2145792	285.8706432
TOTAL		285.8706432		285.8706432

TABLE 4.4: MATERRIAL BALANCE ON COMPRESSOR 1

5. HP COOLER CONDENSER

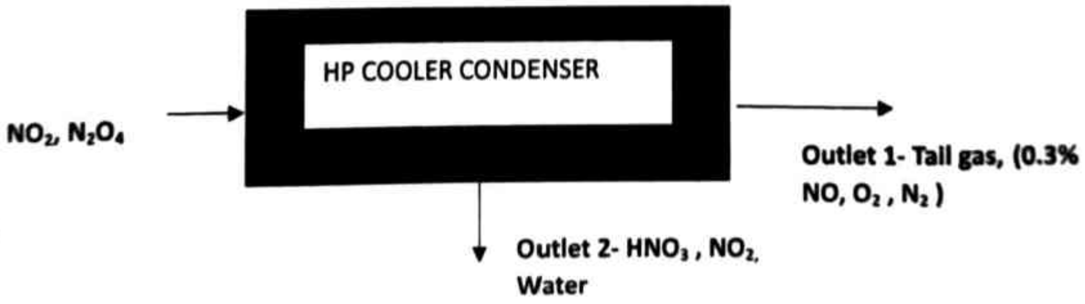


FIG 1.5

GAS PHASE REACTION -
Total conversion = 95%

5.a)$2NO + O_2 \rightleftharpoons 2NO_2$ – (1)

NO Reacted=2.4599376 kmol
O_2 Reacted=1.229988 kmol
NO_2 Produced=2.4599376 kmol

LIQUID PHASE REACTION
Complete conversion to nitric acid

5.b) $3N_2O_4 + 2H_2O \rightleftarrows 4HNO_3 + 2NO$ - (1)
NO_2 reacted=6.2143792 kmol

H_2O reacted=2.0715264 kmol

HNO_3 produced=4.1430528 kmol

NO produced=2.071264kmol

5.b) $3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$ - (2)
N_2O_4 reacted=0.77682604 kmol
H_2O reacted=0.5178816 kmol
HNO_3 produced=1.0357632 kmol
NO produced=0.5178816 kmol

	INLET		**OUTLET(1+2)**	
Component	**Kmol**	**kg**	**kmol**	**kg**
O_2	32.0781	1026.4992	30.8481312	987.1401984
H_2O	149.4951552	2690.912794	146.905742	2644.30345
N_2O_4	0.77682604	71.46799568	-	-
NO_2	6.2145792	285.8706432	2.4599376	113.1571296
HNO_3 -	-	-	5.178816	326.265408
TOTAL		4074.750		4074.750

TABLE 1.5: MATERIAL BALANCE ON HP COOLER CONDENSER

6. ABSORPTION COLUMN

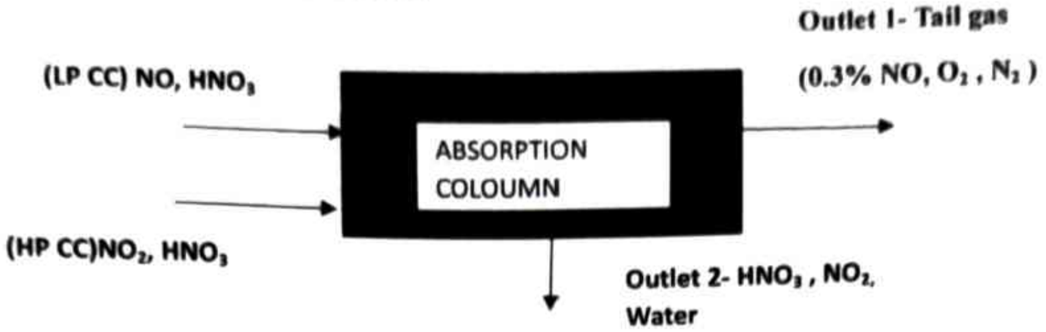


FIG 1.6

VAPOUR PHASE REACTION-

Complete conversion

$2NO + O_2 \rightleftharpoons 2NO_2$ – (1)

NO reacted =1.174824 kmol

O_2 reacted=0.587412 kmol

NO_2 produced=1.174824 kmol

LIQUID PHASE REACTION (1)-

$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$

NO_2 reacted=2.4599376 kmol

H_2O reacted=0.8189792kmol

HNO_3 produced=1.6399584 kmol

NO Produced=0.8199792kmol

HNO3 From condenser=0.7096896kmol

NO From condenser=0.3548448kmol

LIQUID PHASE REACTION (2)-

$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$

NO_2 reacted=1.174824 kmol

H_2O reacted=0.391608kmol

HNO_3 produced=0.783216 kmol

NO produced = 0.391608kmol

	INLET		OUTLET(1+2)	
Component	**Kmol**	**kg**	**kmol**	**kg**
O_2	32.0781	1026.4992	31.29547141	1001.455085
H_2O	149.4951552	2690.912794	148.263568	2699.104224
NO_2	2.4599376	113.1571296	0.390433176	17.9599261
NO	0.3548448	10.645344	0.00174824	0.03524472
HNO_3 -	5.178816	326.265408	7.6019904	478.9253952

TABLE 4.6 : MATERIAL BALANCE OVER ANSORPTION COLUMN

7. DeNO$_X$ REACTOR

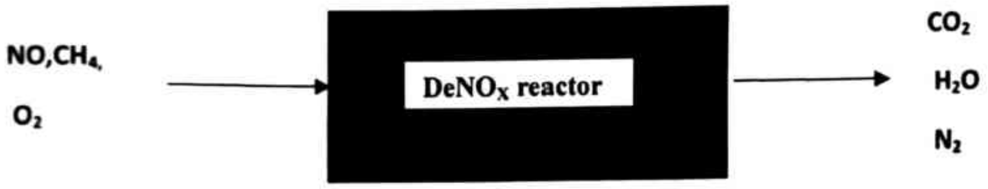


FIG 1.7

7.a)$CH_4 + 2\ O_2 \rightarrow\ CO_2 + 2\ H_20$ - (1)

O_2 Reacted=62.59094282kmol

CH_4 Reacted=31.29547141kmol

CO_2 Produced=31.29547141kmol

H_2O Produced=0.0708944kmol

7.b)$CH_4 + 4\ NO \longrightarrow 2N_2 + CO_2 + 2\ H_20$ – (2)

NO Reacted=0.1417888kmol

CH_4 Reacted=0.0354472kmol

N_2 Produced=0.0708944kmol

CO_2 Produced=0.0354472kmol

H_2O Produced=0.0708944kmol

	INLET		OUTLET	
Component	**kmol**	**kg**	**kmol**	**kg**
N_2	0.7089442	1.9850432	0.7089442	1.9850432
NO	0.1417888	4.253664	-	-
CH_4	31.33091861	501.2946978	-	-
H_2O	-	-	62.66183722	1127.91301
O_2	62.59694282	2002.91017	-	-
CO_2	-	-	31.83091861	1378.560419

TABLE 4.7: MATERIAL BALANCE OVER DeNOx REACTOR

8. EXTENSION OF MATERIAL BALANCE-

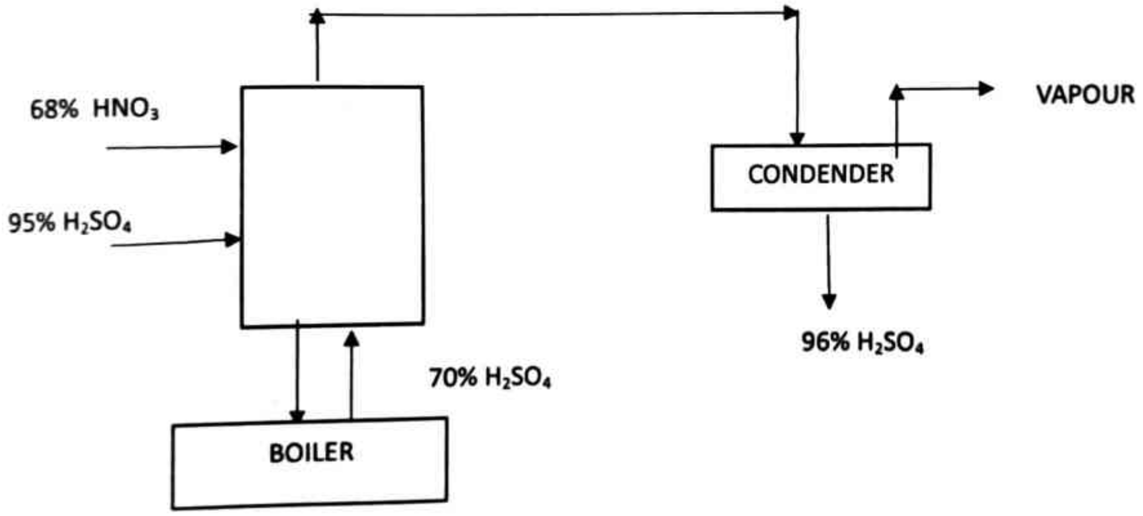


FIG 1.8

Let x= kg, be HNO_3,y=kg,be H_2SO_4,Z=kg,be water

HNO_3 balance-

0.68x+0.28z=1500*0.96=1440

H_2SO_4 balance-

0.93y+0.23z=1500*0.7=1050

H_20 balance-

0.32x+0.07y=1500*0.05=75

x=1187.704188 kg

y= 570.4951419 kg

z= 2258.432687 kg

MODIFIED MATERIAL BALANCE

CAPACITY OF PLANT- 40000 t/year

Working days- 330, rest days are for plant maintenance

Working hours for entire year- 7920 hrs

Nitric acid production per day- 5.05051 t/hr

= 5050.51 kg/hr

= 80.167 kmol/hr

For 100 kmol of Ammonia, acid produced =18.85244742 kmol of nitric acid produced

= 1187.7041188kg of Nitric acid produced.

SCALE UP FACTOR = 5050.51/1187.70411

= 4.3

TOTAL NITRIC ACID PRODUCED= 5107.128008 kg/hr

= 81.065523291kmol/hr

= 5.6296449 t/hr

=135.1114562 t/ day

1. BURNER

	INLET		OUTLET	
	kmol	**Kg**	**kmol**	**kg**
NH_3	430	7310	--	--
O_2	812.7903	26009.29	65.6445	2100.624
N_2	3057.64	85613.91	712.078	19938.184
H_2O	-	-	149.85	2697.3
NO	-	-	95.904	2877.12
N_2O	-	-	0.999	43.956
TOTAL		118932.8		27658.8

TABLE 4.8

2)TG H4, Horizontal boiler, TG H3

	INLET		OUTLET	
Component	**kmol**	**kg**	**kmol**	**kg**
NO	164.95488	4948.6464	-	-
O_2	82.47744	2639.27808	-	-
NO_2	-	-	164.95488	7587.92448
TOTAL	-	7587.92448	-	7587.92448

TABLE 4.9

3) LP COOLER CONDENSER

	INLET		OUTLET(1+2)	
	kmol	**kg**	**kmol**	**kg**
	199.79391	6393.40512	137.93583	4413.94656

H_2O	644.355	11598.39	642.8291674	11570.92501
NO	123.71616	3711.4848	1.52583264	45.7749792
N_2O_4	-	-	16.7016816	1536.554707
NO_2	-	-	85.73529888	3943.823748
HNO_3 -	-	-	3.05166528	192.2549126
TOTAL	-	21703.27992	-	21703.27992

TABLE 4.10

4) NOx COMPRESSOR

	INLET		**OUTLET**	
Component	**kmol**	**kg**	**kmol**	**kg**
N_2O_4	13.36134528	1229.243766	-	-
NO_2	-	-	26.72269056	1229.243766
TOTAL	-	1229.243766	-	1229.243766

TABLE 4.11

5) HP COOLER CONDENSER

	INLET		**OUTLET(1+2)**	
Component	**kmol**	**kg**	**kmol**	**kg**
O_2	32.0781	1026.4992	30.8481312	987.1401984
H_2O	149.4951552	2690.912794	146.905742	2644.30345
N_2O_4	0.77682604	71.46799568	-	-
NO_2	6.2145792	285.8706432	2.4599376	113.1571296

HNO_3 -	-	-	5.178816	326.265408
TOTAL		4074.750		4074.750

TABLE 4.12

6) ABSORPTION COLUMN

	INLET		OUTLET(1+2)	
Component	**Kmol**	**kg**	**kmol**	**kg**
O_2	32.0781	1026.4992	31.29547141	1001.455085
H_2O	149.4951552	2690.912794	148.263568	2699.104224
NO_2	2.4599376	113.1571296	0.390433176	17.9599261
NO	0.3548448	10.645344	0.00174824	0.03524472
HNO_3 -	5.178816	326.265408	7.6019904	478.9253952
TOTAL		4167.519876		4167.519876

TABLE 4.13

7) $DeNO_X$ REACTOR

	INLET		OUTLET	
Component	**kmol**	**kg**	**kmol**	**kg**
N_2	0.7089442	1.9850432	0.7089442	1.9850432
NO	0.1417888	4.253664	-	-
CH_4	31.33091861	501.2946978	-	-
H_2O	-	-	62.66183722	1127.91301

O_2	62.59694282	2002.91017	-	-
CO_2	-	-	31.83091861	1378.560419
TOTAL		2508.458532		2508.458532

TABLE 4.14

CHAPTER 5

ENTHALPY BALANCE

ASSUMPTIONS:

1. Temperature and pressure are fixed balance calculations of many unit operations due to the assumption of saturated steams.
2. The vapor and liquid streams have liquid properties.
3. Kinetic and potential energies of process streams are neglected and only enthalpy changes are considered.
4. Standard enthalpy reference ($\Delta H = 0$) is at $P_0 = 1$ atm, $T_0 = 298K$ and elemental species.

The specific heats of the components are calculated from the following equation:

$$C_p = A + BT^2 + CT^3$$

Component	**Phase**	**A**	**B**	**C**
Water	**Gas**	30.415	9.26×10^{-3}	-1.196×10^{-6}
	Liquid	29.16	14.49×10^{-3}	-2.02×10^{-6}
NH_3	**Gas**	61.289×10^{-3}	80.925×10^{-3}	799.4×10^{-3}
	liquid	25.48	36.89×10^{-3}	-6.305×10^{-6}
NO	**Gas**	-2979600×10^{-3}	76602×10^{-3}	-652.59×10^{-3}
N_2O	**Gas**	67996×10^{-3}	34.373×10^{-3}	-
O_2	**Gas**	175430×10^{-3}	-6152.3×10^{-3}	113.92×10^{-3}
N_2	**Gas**	27.31	5.2335×10^{-3}	-4.1868×10^{-9}
CO_2	**Gas**	26.75	42.26×10^{-3}	-14.25×10^{-6}
CH_4	**Gas**	13.41	7.703×10^{-3}	-18.74×10^{-6}
HNO_3	**Gas**	19.63229	153.9599	-115.8378
	Liquid	110	-	-
NO_2	**Gas**	24.23	4.84×10^{-3}	-20.81×10^{-2}

N_2O_4	**Gas**	$89.1013x10^{-3}$	$178.9141x10^{-3}$	-

TABLE 4.15: VALUES OF CONSTANTS FOR DIFFERENT COMPOUNDS

5.1) ENTHALPY BALANCE OVER VAPOURISER-

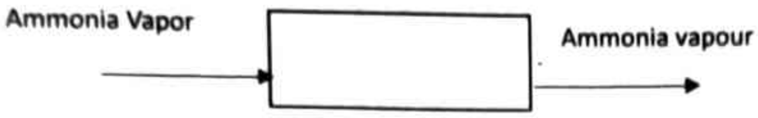


FIG 2.1

Temperature = 238K to 343K

Pressure=12-15 bar

ΔH_{NH3}, in= 0

ΔH_{NH3} , out = n$\int CpdT$

$$= 100 * 4.3 \int_{238}^{343} [25.48 + (36.84 * 10^{-3})T - 6.305 * 10^{-6}T^2] \, dT$$

=11377518.78 KJ/kmol

Δ H generation = Δ Hout- Δ Hin = 11377518.78 KJ/kmol

5.2) COMPRESSOR-

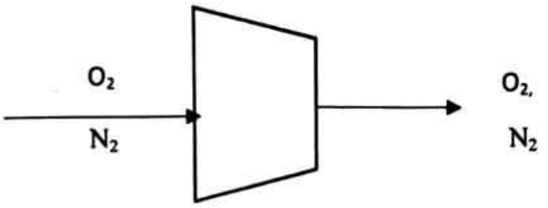


FIG 2.2

ΔHN_2, in = 0 , ΔN_2, in = 0

ΔHN_2, out = n$\int CpdT$

$$=3057.6397 \int_{298}^{513} [227.31 + 5.2335 * 10^{-3}T - 4.18688 * 10^{-9}] dT$$

=19348035.05kJ/kmol

$$\Delta HO_2, \text{out} = 812.7903 \int_{298}^{513} [175430 * 10^{-3} + 6152.3 * 10^{-3}T - 113.92 * 10^{-9} T^2] dT$$

= 2944779969 KJ/kmol

$\Delta H_{out,\ total}$ =2964128004 KJ/kmol

$\Delta H_{generation}$ = 964128004 KJ/kmol

5.3) ENTHALPY BALANCE OVER MIXER-

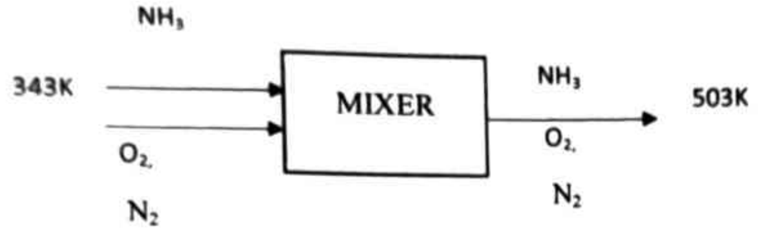


FIG 2.3

ΔHNH_{3in} = 11377518.78 K/kmol
$\Delta HN_{2,in}$ = 19348035.05 KJ/kmol

$\Delta HO_{2,\ in}$ = 2944779969 KJ/kmol

$\Delta HNH_{3\ ,\ out} = n\int CpdT$

$$= 100 * 4.3 \int_{343}^{503}[61.289 * 10^{-3} + (80.925 * 10^{-3})T + 799.4 * 10^{-3}T^2]dT$$

= 9966555902 KJ/kmol

ΔHN_2, out=$3057.6397 \int_{513}^{503}[27.31 + (5.2335 * 10^{-3})T + 4.1868 * 10^{-3}T^2]dT$

=-916299.3239 KJ/kmol

ΔHO_2, out=$812.7903 \int_{513}^{503}[175430 * 10^{-3} - (6152.3 * 10^{-3})T + 113.92 * 10^{-3}T^2]dT$

= -26828808.17 KJ/kmol

Total ΔH_{OUT} = 9932810795 KJ/kmol

ΔH generation = 6957305272 KJ/kmol

5.3) ENTHALPY BALANCE OVER REACTOR-

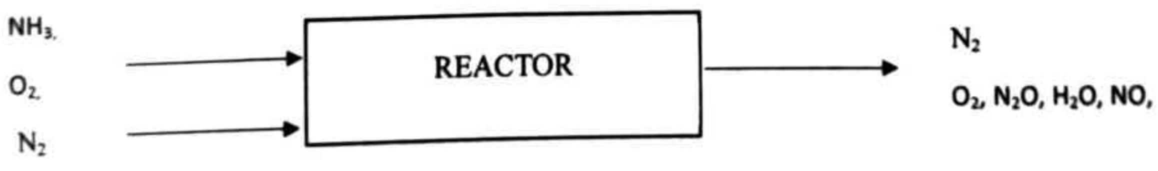


FIG 2.4

3.a)$2NO + O_2 \longrightarrow 2NO_2$ ---- (1) (Conversion to NO_2 - 50%)

ΔH_R° 298 = -226334 KJ/kmol K

ΔH°_{298} = -226,334 KJ/mol

$\Delta H^{\circ}_T = \Delta H' + \Delta\alpha T + \alpha\beta\gamma T^2/2 + \Delta\gamma T^3/3$

$\Delta\alpha$ = -489.504189

$\Delta\beta$ = -183.4019309

$\Delta\gamma$ = -1.5923815

$\Delta H'_{298}$ = 22109928.64 KJ/mol

ΔH°_{1163} = -104194039.4 KJ/mol

3.b) $4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$ ------- (2)

ΔH_R° 298 = -310776 KJ/kmol K

$\Delta H^{\circ}_{R.}$ 298 = -452435 KJ/mol

$\Delta\alpha$ = -96.000789

$\Delta\beta$ = 6.8065615

$\Delta\gamma$ = -0.9613115

$\Delta H'_{298}$ = 7312806.865 KJ/ mol

ΔH°_{1163} = -452435 KJ/mol

3.c) $4NH_3 + 4O_2 \longrightarrow 2N_2O + 6H_2O$ ------ (3)

ΔH_R° 298 = 452435kj/kmol K

ΔH°_R= -316,776 KJ/kmol

$\Delta\alpha$ = -414.544946

$\Delta\beta$ = 6.196425

$\Delta\gamma$ = -9.8580375

$\Delta H'_{298}$ = 86244250.05 KJ/kmol

ΔH°_{1163} = -4301902127 KJ/ kmol

$\Delta H^{\circ}_{1163,\ \text{generation}}$ = -186642130.1 KJ/ kmol

$\Delta H_{in,\ O2} = 282.27135 \quad \int_{503}^{298}(175430 \times 10^{-3} - 6152.3 \times 10^{-3}T + 113.92 \times 10^{-3}T^2)dT$

= 457486628 KJ/ kmol

$\Delta H_{in\ N2} = 3061.9354\ \int_{503}^{298}(27.31 + 5.2335 \times 10^{-3}T + 4.1868 \times 10^{-9}T^2)dT$

$= 46373956.69$ KJ

$\Delta H_{NH3.\ in} = 430\ \int_{503}^{298}(61.289 \times 10^{-3} + 80.925 \times 10^{-3} + 799.4 \times 10^{-3}T^2)dT$

$= 385315277.8$ KJ

$\Delta H^{o}_{R.\ 1163} = -186642130.1$ KJ

$\Delta H^{o}_{in} = 1847939860$ KJ

$\Delta H_{N2.\ out} = 3061.9354\ \int_{298}^{1163}(27.31 + 5.2335 \times 10^{-3}T + 4.1868 \times 10^{-9}T^2)dT$

$= 118946348.8$ KJ

$\Delta H_{O2.\ out} = 282.27135\ \int_{298}^{1163}(175430 \times 10^{-3} - 6152.3 \times 10^{-3}T + 113.92 \times 10^{-3}T^2)dT$

$= 4829185053$ KJ

$\Delta H_{NO.\ out} = 412.3872\ \int_{298}^{1163}(-2979600 \times 10^{-3} + 76608 \times 10^{-3}T - 652.59 \times 10^{-3}T^2)dT$

$= 4.204919692 \times 10^{11}$ KJ

$\Delta H_{N2O.\ out} = 4.2957\ \int_{298}^{1163}(67556 \times 10^{-3} + 54.37 \times 10^{-3}T)dT$

$= 315935.9909$ KJ

$\Delta H_{H2O.\ out} = 644.355\ \int_{298}^{1163}(30.475 + 9.62 \times 10^{-3}T - 1.196 \times 10^{-6}T^2)dT$

$= 30012404.83$ KJ

$\Delta H_{out} = -4.155135095 \times 10^{11}$ KJ

Total generation = -41249556640 – 390354.1251 – 184796809.7

$= -4.14347438 \times 10^{10}$ KJ

In + Generation = Out + Accumulation

⇨ Accumulation = -35432168850 KJ

Steam from steam drum utilizes this energy. Therefore, amount of steam required is

$$n = \frac{35432168850}{1.966 \times 1163.503}$$

= 27306767.2 Kmol/hr

= 491521809.6 Kg/hr

5.4) ENTHALPY BALANCE ON HEAT EXCHANGER (Tail gas Heater 4, horizontal boiler + economiser)

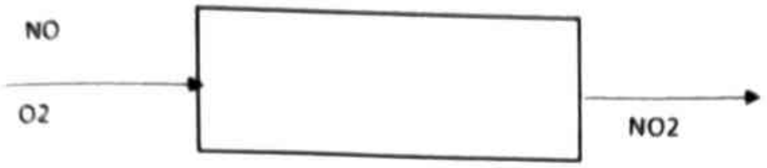


FIG 2.5

4.a) $2NO + O_2 \longrightarrow 2NO_2$ ------(1) (Conversion- 40%)

$\Delta\alpha = \alpha_{NO2} - \frac{1}{2}\alpha_{O2} - \alpha_{NO2}$

$= -63.48202034$

$\Delta\beta = \beta_{NO2} - \frac{1}{2}\beta_{O2} - \beta_{NO}$

$= -73.47745$

$\Delta\gamma = \gamma_{NO2} - \frac{1}{2}\gamma_{O2} - \gamma_{NO}$

$= 0.38753$

Limiting Reagent = NO

For 2kmol of NO energy required = -9236742.811 KJ/mol

Therefore, 164.95488 kmol of NO energy required = $\frac{-9236742.811 \times 164.9545}{2}$

$= -761822901$ KJ

For 40% conversion = -304729160.4 KJ

$\Delta H'_{298} = -6604986.695$

$\Delta H_{408} = -9236742.811$ KJ

$\Delta H_{NO,\,in} = m\int_{1163}^{298} Cp\,dT$

$= 164.95488 \int_{1163}^{298}(-2979 \times 10^{-3} + 76602 \times 10^{-3}T - 652.59 \times 10^{-3}T^2)dT$

$= 46514321780$ KJ

$\Delta H_{O2,\,in} = m\int_{1163}^{298} Cp\,dT$

$= 82.47744 \int_{1163}^{298}(175456 \times 10^{-3} - 6152.3 \times 10^{-3}T + 113.92 \times 10^{-3}T^2)dT$

$= -4423946164$ KJ

$\Delta H_{in,\,total} = 420903756.21$ KJ

$\Delta H_{NO2,\ out} = m \int_{298}^{408} CpdT$

$= 164.95488 \int_{298}^{408}(24.23 + 4.84 \times 10^{-2}T - 20.81 \times 10^{-2}T^{2})dT$

$= -2328445340$ KJ

Input + Generation = Output + Accumulation

- ⇨ 42090375621 – 304729160.4 = -2328445340 + Accumulation
- ⇨ Accumulation = 4597620666 KJ

Boiler feed water utilizes this energy

- ⇨ -4597620666 = m × 4.186 × (408 – 1163)
- ⇨ m = 13958256.25 kmol/hr
- ⇨ m = 251248612.5 kg/hr

5.5) ENTHALPY BALANCE ON LP COOLER CONDENSER

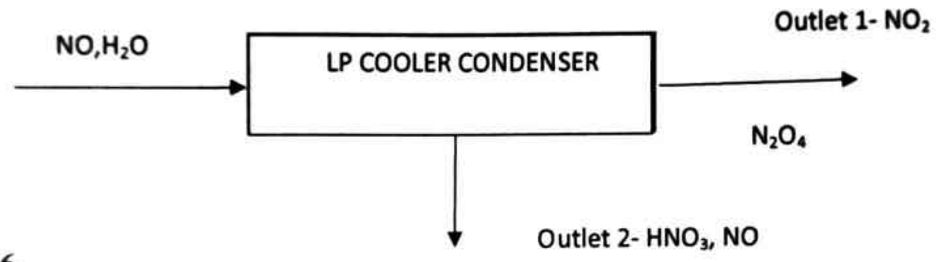


FIG 2.6

5.a) $2NO + O_2 \rightleftharpoons 2NO_2$-------(1)

ΔH_R° 298 = 57120kj/kmol K

Δα=- 63.48202039

Δβ= -73.47745

Δγ = 0.38753

ΔH' 298 = -6604986.695

AT 408 K

ΔHT °=-9236742.811Kj

Here limiting reactant =NO

2 kmol NO, energy required =-7023748.865kJ/kmol

For 123.7166 kmol of NO,

$\Delta H_{NO,\ in} = n \int_{408}^{298} CpdT$

-123.71616 $\int_{408}^{298}(-297600 \times 10^{-3} + 76602 \times 10^{-3}T - 692.59 \times 10^{-3}T^2)dT$

= 649449331kJ

ΔH, $O_{2,\ in}$= 61.85808 $\int_{408}^{298}(175430 \times 10^{-3} - 6192.3 \times 10^{-3}T + 113.92 \times 10^{-3}T^2)dT$

= -72541892.23 kJ/kmol

ΔH, $H_2O_{,in}$ = 1.2371616 $\int_{408}^{298}(30.475 + 9.62 \times 10^{-3} - 1.196 \times 10^{-6T^2})dT$
=-3764.4694 kJ/kmol

$\Delta H_{NO2,out}$ =$n \int_{298}^{318} CpdT$
=123.71616 $\int_{298}^{318}(24.23 + 4.84 \times 10^{-2}T - 20.81 \times 10^{-2}T^2)dT$
=-812316122.29Kj
$\Delta H_{N2O2,out}$ =$n \int_{298}^{318} CpdT$

=18.557424 $\int_{298}^{318}(89.1013 \times 10^{-3} + 178.9141 \times 10^{-3}T)dT$

=336276.1791 kJ

$\Delta H_{HNO3,out}$ =n$\int Cp\ dT$
=3.05166528 $\int_{298}^{318} 110\ dT$
=86513.65536 kJ

$\Delta H_{NO,\ out}$ = n$\int Cp\ dT$
= 318 × 1.2371616 $\int_{298}^{318}((-2979600 \times 10^{-3} + 76602 \times 10^{-3}T - 652.59 \times 10^{-3}T^2)dT)$

ΔH_{in}=6421907439kJ/kmol

ΔH_{OUT}=-84657949.03 kJ/kmol

5.b) $2NO_2 \rightleftarrows N_2O_4$ ------ (2)

$\Delta H_R°$ 298 = 57.32 KJ/kmol K

$\Delta\alpha$=- 24.18541844

$\Delta\beta$=0.0410570
$\Delta\gamma$ =28.81×10^{-2}

$\Delta H_{298,R}$=57.32 KJ/kmol

For 2 kmol . ΔH_{318}=729475.458 KJ/kmol

For 37.1148 kmol, $\Delta H318$=13537167.88 KJ
=$89.163\times0.5\times 10^{-3}$

5.c) Liquid phase reaction-

$3N_2O_4 + 2H_2O \rightleftharpoons 4HNO_3 + 2NO$ -----(3)

$\Delta\alpha$= -1949.21313

$\Delta\beta$=51.06158869

$\Delta\gamma$ =-0.4342626

$\Delta H'_{298}$ =2255997.071 KJ/kmol

ΔH^0_{318}=-43700 KJ/kmol

Here L.R =N_2O_4
$\Delta H_{Q,248}$=-437000 KJ/kmol
For 1.8557424kmol, ΔH^0_{318}=810959.4288 KJ
For 10% conversion= 81095.94288 KJ
ΔH^o_R 298 = -437,000Kj/kmol K

5.d) $3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$ ---- (4)

ΔH^o_R 298 = -58700 KJ/kmol K

$\Delta\alpha$= -953.8167

$\Delta\beta$=15.327267

$\Delta\gamma$ =0.0126367

$\Delta H'_{298}$ =-723579.7063 KJ/kmol

ΔH^0_{318}=-116461.5358 KJ/kmol

Here LR=NO_2
For 3 mol, ΔH^0_{318}=-116461.5358 KJ/kmol
For 0.86601312 kmol, ΔH^0_{318}=-33619.07266 KJ
For 10% conversion= -3361.907266 KJ

This is used by cooling water flowing in the condenser
$Q = n\int CpdT$

⇒ 6247915885 = m×4.186 × (318.298)

⇒ m = 7462871.39 kmol/ hr

= 13443316 kg/hr

Input + Gen= Output + Accumulation

Accumulation = -6076228.653 KJ/kmol

Cooling water utilizes this energy.

∴ 6076228.653=m×4.186×(408-318)

⇒ m =16128.44 kmol/hr

= 290311.928 kg/hr

5.6) ENTHALPY BALANCE NOX COMPRESSOR

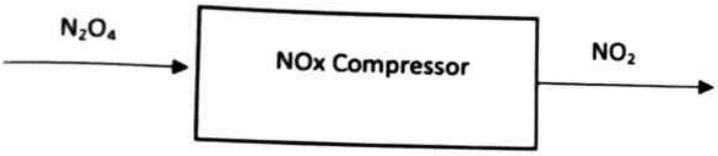


FIG 2.7

6.a) $2N_2O \rightleftharpoons$ $2NO_2$ (Conversion- 80%)

ΔH°_R 298 = 287300 KJ/kmol K

$\Delta\alpha$= 48.37063

$\Delta\beta$= -0.0821141

$\Delta\gamma$ =-0.4162

$\Delta H'$ 298 = 3947913.853 KJ/kmol

ΔH497=-13069573.11 KJ/kmol

FOR LIMITING REAGENT N_2O_4, ΔH_R 497= -13069573.11 KJ /kmol

FOR 13.36134 kmol, ΔH_R 197=174627010 KJ

FOR 80% CONVERSION = 13970168 KJ

ΔH_{in}, $N_2 0_4 = n \int_{310}^{298} CpdT$

$$=13.36134\int_{318}^{298} (89.16313 \times 10^{-3} + 178.9141 \times 10^{-3}T)d$$

$$=-38552.455 \text{ KJ}$$

ΔH_{OUT}. $NO_2 = n \int_{298}^{497} CpdT$

$$-26.7226 \int_{298}^{497} (24.23 + 4.84 \times 10^{-2}T - 20.81 \times 10^{-2}T)dT$$

$$= -1782758.553 \text{ KJ}$$

ΔH_{in} =-38552.455 KJ/kmol
ΔH_{OUT}=-1782758.553 KJ/kmol
ΔH_{gen} = 13970168 KJ/kmol

Input + Gen= Output + Accumulation

⇒ Accumulation=15714374.1 KJ/kmol

5.7) ENTHALPY BALANCE ON HP COOLER CONDENSER

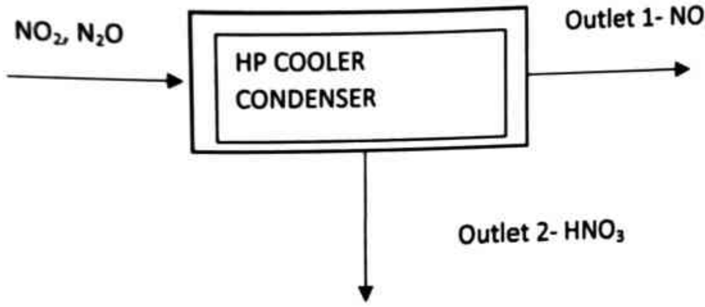


FIG 2.8

7. a) $3N_2O_4 + 2H_2O \rightleftharpoons 4HNO_3 + 2NO$ ----- (1)

$\Delta H°_R$ 298 = -437000Kj/kmol K

$\Delta H_{295,B} = \Delta H^1 + \Delta\alpha T + \alpha\beta \frac{T^2}{2} + \alpha\gamma\frac{T^3}{3}$

$\Delta\alpha$ = - 5574.78

$\Delta\beta = \Delta\beta_{HNO_3} + 4\beta_{NO} - 3\beta_{N_2O_4} - 2\beta_{H_2O}$

= 305.8520

$\Delta\gamma = \Delta\gamma_{HNO_3} + 4\gamma_{NO} - 3\gamma_{N_2O_4} - 2\gamma_{H_2O}$

= -2.58644

ΔH^1_{2AB} = 1046023.77 KJ/KMOL

ΔH^O_{368} = -13847841.76 KJ/KMOL

Here LR = N_2O_4

3 mol of $N_2\,O_4$ requires energy = -13847841.76 KJ/kmol

Therefore 3.340351 mol of $N_2\,O_4$= -13847841.76 x 3.340351 / 3

= - 15418884.02 KJ

$\Delta H_{im,N_2\,O_4}$ = m $\int_{368}^{298} C_p\, dT$

=3.340351 $\int_{368}^{298}(189.16313 \times 10^3 + 178.9141 \times 10^3\, T)dT$

= -13951.7411 KJ

$\Delta H_{NO,in}$ = n$\int_{368}^{298} Cp\, dT$

= 2.22689 $\int_{368}^{298}(-2979600 \times 10^3 + 76602 \times 10^{-3} T - 652.54 \times 10^3\, T^2)\, dT$

= -2346040.306 KJ

$\Delta H_{out,HNO_3}$ = n $\int_{298}^{323} Cp\, dT$

= 4.4531 $\int_{298}^{323} 110\, dT$

= 12247.675 KJ

$\Delta H_{NO_2,OUT}$ = $\int_{298}^{323} Cp\, dT$

=26.72269 $\int_{298}^{323}(24.23 + 4.48 \times 10^{-2} T - 20.81 \times 10^{-2}\ T^2\ )dT$

= 4256991.897 KJ

7.b) $3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO$ ---- (2)

$\Delta H_T^0 = \Delta H^1 + \Delta\alpha T + \alpha\beta \frac{T^2}{2} + \alpha\gamma\frac{T^3}{3}$

$\Delta\alpha$ = 185.70

$\Delta\beta$ =76.4423

γ = -1.2379

ΔH^0 =7411530.13

ΔH_{323}^0= 7411530.13 + 185.70 x 323 + 76.44231 x $\frac{323^2}{2}$ – 1.2379 x $\frac{323^2}{2}$

= -2445942.13 KJ/kmol

LR: NO_2

For 3 mol NO_2, energy required =- 2445942.134 KJ/kmol

For 26.72269 kmol, energy required = - 21787384.43 KJ

ΔH_{in}= -13951.7411-2346040.308

=-2359992.047 KJ

ΔH_{out} = 12247.675+ 42568991.897

= -4269239.572 KJ

ΔH_{gas}= -13847841.76 - 2445942.13

=-16293783.89 KJ

Accumulation= 22923045.91 KJ

This energy is used by cooling water inside the condenser

$n= -\frac{-22923015.51}{1.486\,x(323.368)}$ =342794.6936 kmol/hr

= 6170394.485 kg/hr

5.7) ENTHALPY BALANCE ON ABSORPTION COLUMN

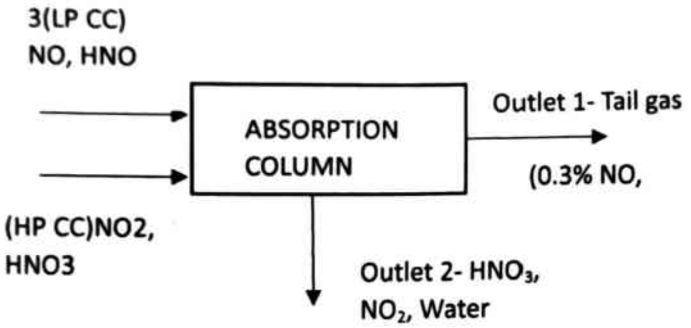


FIG 2.9

8.a) $3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$ ----- (1)

$\Delta\alpha$ = - 953.81

$\Delta\beta$ =15.327

$\Delta\gamma$ = -0.012637

Here LR = NO_2

3 kmol of NO_2, ΔH^0_{323} =-123579.7063 KJ/kmol

For 10.3771 MOL of NO_2 , ΔH^0_{323} = -5618086.998 KJ/kmol

8.b) $2NO + O_2 \rightleftharpoons 2NO_2$ ----- (2)

$\Delta\alpha$ = - 66.432020

$\Delta\beta$ =-73.47745

$\Delta\gamma$ = -0.38753

ΔH^1_{298}= -7134812.992 KJkmol

ΔH^{1}_{288} = -21456792.33 KJ/kmol

Here LR = NO

2 kmol of NO, =214567592.33 KJ/kmol

For 1.5258 KMOL of NO = 163665159.55 KJ/Kmol

8.c) $3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO$ ----- (3)

$\Delta H_{IN,HNO_3} = m \int_{323}^{298} Cp\, dT$

$= 22.268 \int_{323}^{298} 110\, dT$

= 61237 KJ

$\Delta H_{NO,IN} = m \int_{323}^{298} C_p\, dT$

$= 1.5258 \int_{323}^{298} (-2979600\, x\, 10^{-3} + 76602\, x\, 10^{-3}\ \ T - 652.59\, x\, 10^{-3})\, dT$

= 5501499.019 KJ

$\Delta H_{NO,IN} = m \int_{323}^{298} C_p\, dT$

$= 10.5771 \int_{323}^{298} (24.23 + 4.34\, x\, 10^{-2} T - 20.81\, x\, 10^{-2})\, dT$

ΔH_{in} = 807648720.1 KJ

$\Delta H_{NO_2,OUT} = \int_{298}^{288} Cp\, dT$

$= 5.05164 \quad \int_{298}^{288} (.297960\, x\, 10^{-3} + 76602\, x\, 1o^{-3} T - 652.59\, x\, 10^{-3}\ T^2\ )dT$

= 1412323.122131 KJ

$\Delta H_{out,HNO_3} = n \int_{298}^{288} Cp\, dT$

$= n \int_{298}^{288} 110\, dT$

= -35957.35 KJ

ΔH_{out} =1376365.772KJ

Total generation = 15242898.56 KJ

Input generation = output + accumulation

Accumulation = 94631352.89 KJ

Cooling water is used for circulation in the tower

-94631352.89 = m × 1.486 × (288-298)

=> m = 6368193.33 Kmol/hr

= 114627479.9 kg/hr

CHAPTER 6

EQUIPMENT DESIGN

6.1 DESIGN OF NITRIC ACID STORAGE TANK

TOTAL NITRIC ACID PRODUCED = 5107.128008 kg/hr

= 1838566.083 kg/month

THE VOLUME OF HNO_3 = 1294.764847 m^3

10% VOLUME ADDED

DENSITY OF NITRIC ACID=1420 kg/m^3

FOR 15 DAYS THE VALUME OF HNO3 =1424.24133 m^3

ASSUMPTION-

C1= ANNUAL COST OF FABRICATING OF SHELL PER UNIT AREA = 2C2

C2 = ANNUAL COST OF FABRICATING OF BOTTOM PER UNIT AREA

C3 = ANNUAL COST OF FABRICATING OF ROOF PER UNIT AREA = 1.8C2

C4 = ANNUAL COST OF INSTALLED FOUNDATION UNDER THE VESSEL

C5 = ANNUAL COST OF INSTALLATION COST C5 ESTIMATED AS 0.4 TIMES OF THE COST OF THE BOTTOM AREA IN C2.

C1 = 2C2

C3 = 1.8C2

C4+C5 = 0.4C2

T = UPTO 250^{0}C, IS = 2002-1962, 2B, Pressure-150-200 psi

ASSUMING A SMALL TANK

THEN THE OPTIMUM TANK PROPORTION

D/H = 2C1/(C2+C3+C4+C5)

= 4C2/(C2+1.8C2+0.4C2)

D = 1.25 H

V=3.14D2H/(4)

H = 13.24040362 m = 43.43964442 ft

$D = 16.55050453$ m $= 54.29955553$ ft

ASSUMING DOUBLE WELDED BUTT JOINT, CONDITION FOR SMALL TANK IS

$D(H-1)<1720$,D AND H ARE in

$2304.453829 > 1720$

IT DOES NOT SATISFY THE SMALL TANK ASSUMPTION

NOW, ASSUMING BIG TANK ASSUMPTION

$D/H = 4C1/(C2+C3+C4+C5)$

$D = 2.5H$

$H=8.340931616$m$=27.36526121$ft

$D=20.85232904$m$= 68.41315302$ ft

$D(H-1)>1720$

1 803.730649>1720 ft

IT SATISFY THE LARGE TANK ASSUMPTION

$g=1$ (assumed)

$E=0.85$(DOUBLE WELDED BUTT JOINT)

$S=1200$ kgf/cm2 (TYPE 360L AND 340L STAINLESS STEEL) [IS 4560:1968]

APPENDIX (CLAUSE 2.2.1.1)

TABLE A-1.1

TO FIND THE NUMBER OF PLATES TO BE THERE, ALLOWING A GAP OF 2 mm FOR EACH JOINTS THE TOTAL ALLOWANCE

FOR THE JOINT WILL BE 2×10^{-3}

CIRCUMFERENCE = $3.14D-2n\times10^{-3}/n$

LENGTH OF THE PLATE, $L=3.14D-2n\times10^{-3}/n$

$n=7$, $L = 9.356503389$ m

WE CONSIDER $n = 7$ no. of plates

$W=H/n= 1191.561659$ millimetre

W_{stdard} VALUE =1250 mm = 1.25mm [APPENDIX B-(STANDARD VALUE) TABLE B-1 STEEL PLATER]

THICKNESS OF THE FIRST SECTION

$t1= 50(H-0.3)\,DG/(SE)$

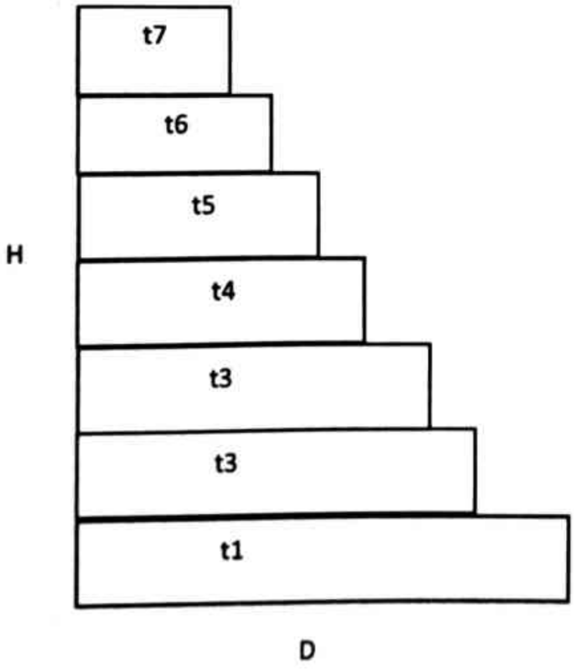
CORROSION ADDED = 0.3 mm

DATA TAKEN FROM BC BHATTACHARYA APPENDIX A

THICKNESS SECTION	t(mm)	tc'(mm)	t_{std}
t1	8.151295666	8.451295666	9mm
t2	6.584139064	6.884139064	7mm
t3	5.616982462	5.916982462	6mm
t4	4.34982586	4.64982586	5mm
t5	3.08266925	3.08266925	5mm
t6	1.615512654	1.915512654	5mm
t7	0.5483560547	0.8483560547	5mm

DATA TAKEN FROM 6.3.3.2 OF IS: 803, 1976, PAGE NO. 23

NOMINAL TANK dia, m	MINIMUM THICKNESS, mm
OVER 15 UPTO 36	6.0



6.2 DESIGN OF SHELL AND TUBE HEAT EXCHANGER

STEP1) ASSUMING-

Shell side	Tube side
ID=8 in, Passes=1 Baffle space=14 in	OD=1.25in,BWG=0.165,ID=0.920 in, Flow area per tube in inch square=0.665 Passes=8

We use 1 in OD tubes 1.25 triangular pitch. [ALL DATAS ARE TAKEN FROM D Q KERN BOOK]

R_d given=0.002 [3]

We assume the value of U (overall heat transfer coefficient) to be 300 W/m^2

STEP 2)-Heat balance-

Heat capacity of nitric oxide = 1.066 kJ/kg. K

Nitric oxide flow rate = 0.827 kg/s

Inlet temperature of nitric oxide = 150^0C

Outlet temperature of nitric oxide = 50^0C

Heat load = 0.827 x 1.066 x (150 - 50) KW = 88.1582 KW

Heat capacity of water = 4.195 kJ/kg K

Water flow rate = 0.744 kg/s

ΔT (water) = 88.1582/ (0.744x4.195) = 28.246^0 C

STEP3)-LMTD

LMTD = ((150-63.246)-(50-35))/ ln (86.754/15) = 40.88

R = T1 – T2/(t2 – t1) = 100/28.246 = 3.54

S = t2 – t1/(T1 – t1) = 28.246/115 = 0.2456

From graph, Ft = 0.8

ΔT_l= 0.8 x 40.88 7

Total area of heat transfer A Q/(UxΔTm) = 8.98 m^2

STEP4)- TEMPERATURE

μ (water) = 0.024cp < 1cp

μ (Nitrous oxide) = 0.038<1cp

$\Delta T_{average} = 32.704^OC$

We assume the value of U (overall heat transfer coefficient) to be 300 W/m^2

Total area of heat transfer A Q/ (U x ΔTm) = 8.98 m^2

Area of 1 tube = 3.14 x do x L = 0.303 m^2

No. of tubes= A/ (Area of 1 tube) = 29.62 tubes 30 tubes Db = 20 * (30/K1) 1/n 1 = 20 * (30/0.249)1/2.207 = 175.349 mm

Diametrical clearance = 50 mm Shell diameter

Ds = 175.349 + 50 = 225.349 mm

STEP5) -PROPERTY

Property	Water	Nitrous oxide
μ	0.024 x10^{-3} Pas	0.038 x10^{-3} Pas
K	0.330 W/m. K	0.042 W/m. K
C_P	1.066 x 10^3	0.024x10-3 N sec/ m^2
P	995 kg/m3	1.249 kg/m^3

STEP 5) - Tube and Shell coefficients

Mean water temperature = (35 + 63.246)/2 = 49.123 C

Tube cross sectional =area π/ x di 2 = 3.14/4 x (162) = 201 mm^2

Tubes per pass = 30/2 = 15 tubes

Total flow area = 15 x 201 x 10-6 = 3.015 x 10-3 = 0.003015 m^2

Mean shell side temperature = (150 + 50)/2 = 100^O C

As nitrous oxide is corrosive so it is passed through the tube side.

STEP6) - h_i and h_o calculation

TUBE SIDE(NITROUS OXIDE)	SHELL SIDE(WATER)
1) Mass velocity, Gs = 0.827/0.002521 = 328.044 kg/s m 2)Cross flow area At = ((25-20)/25) x (251.049 x 50.2098 x 10-6) = 2.521 x 10-3 m^2 3) Tube pitch = 1.25 x 20 = 25 mm 4)Equivalent diameter, de = 1.1/20 x (252 - 0.917 x 202) = 14.4 mm 5)Re = Gt*de /μ = 328.044x14.4x10-3 /0.024x10-3 = 196826.4	1) Water mass velocity = 0.744/(0.00603) = 123.38 Kg/m^2 .s 2) Tube cross sectional area = 3.14/4 x (162) = 201 mm^2 3) Tubes per pass = 60/2 =30 tubes 4) Total flow area = 30x 201 x10-6 = 6.03 x10-3 = 0.00603 m 2 5) Mean water temp. =

7) From graph, jh = 3.4 x 10-3 (Page no. 665, Coulson & Richardson [17]) = 90.471 ^{O}C 8)Nu = hsde /kf= jhRePr1/3 9) hi = 0.04/0.0144 x (3.4 x10-3 x 196826.4 x 0.63961/3) = 1601.63 W/m^{2}K	(35+63.246)/2 = 49.123^{0}C 7)Water linear velocity = 123.38/995 = 0.124 m/sec 8) h_S = 4200 x (1.35 + 0.02t) x ut 0.8/(di 0.2) = 4200 x (1.35+ 0.02 x 49.1) x 0.1240.8/(160.2) = 1059.197 W/m^{2}K

Overall coefficient

Thermal conductivity of cupro-nickel alloy = 50 W/m.K

Fouling coefficient for water = 3000W/m^{2}K

Fouling coefficient for nitric oxide = 5000 W/m^{2}K

1/U0 = 1/h_o + 1/h_{od} + (do/di) x 1/hid + (do/di) x 1/hi 1/Uo = 1/1638.01 + 1/5000 + (20x10-3 x ln(20/10))/2x50 + (20/16)x(1/3000) + (20/16) x (1/1844.169)

Uo = 513.05 W/m^{2}K

A = 9.21m^2

Rd_{cal} =0.00251

$Rd_{cal} > Rd_{given}$

This value is well above the assumed value of 300W/m^{2}K.

Thus, the design is satisfactory.

STEP-7) PRESSURE DROP

Pipe side pressure drop-	Annular side pressure drop-
1)Re = 196826.4 2) f = 2.9 x 10-2 3)ΔPs = 8 x jFx(Ds/de) x (L/IB) x (ρus 2 /2) ΔPs = 8 x 2.9 x 10-2 x (251.049/14.4) x (2.39x103 /50.2098) x 1.249 x 26.2642 /2 = 8.2719<10 psi	1)Re =ρudi /μ 995x 1 x16x10 $^{-3}$ /0.001 = 1974.08 2)f = 3.9x10^{-2} 3)ΔPt = 2 x (8 x 3.9 x 10-2 x (2.39 x 103 /16) + 2.5) x 995 x 0.1242 /2 = 751.26 N/m^2 = 0.751 kPa As this value is low we could consider increasing the number of

	passes to 6 Tubes per pass = 60/6 = 10 Total flow area = 10 x 201 x 10-6 = 201 x 10-5 m^2 4)ΔP_s = 6 x (8 x 1.5 x 10-2 x 2.39x103 /16 + 2.5) x 995 x 0.3722 /2 = 8437.08N/m^2 = 2.42 psi<10 psi

Therefore, Pressure drop are less than 10psi, so the design is correct.

CONCLUSION

Nitric Acid is an important chemical compound from economical point of view. During this project our job was to study the development and designing of the complete process and also the equipment used. Proper raw material, optimum efficiency, safety and economy of the plant have also been looked into. In performing this project we have calculated the capacity of a storage tank to store the product for 15 days.

The production of nitric acid is a complex process that involves the oxidation of ammonia followed by the absorption of nitrogen dioxide in water. This versatile chemical plays a vital role in various industries, but its production requires careful attention to safety, environmental impact, and energy efficiency. Continued research and technological advancements aim to improve process efficiency and reduce environmental emissions associated with nitric acid production.

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MANUFACTURE OF ETHANOL

Submitted in the partial fulfilment of
The Requirements for degree of

Bachelor of Technology

in

Chemical Engineering

under

Assam Science and Technology University (ASTU)

SUBMITTED BY:

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B.Tech 8th SEMESTER

DEPARTMENT OF CHEMICAL ENGINEERING
ASSAM ENGINEERING COLLEGE
JALUKBARI, GUWAHATI-13
SESSION 2022-23

CERTIFICATE
DEPARTMENT OF CHEMICAL ENGINEERING
ASSAM ENGINEERING COLLEGE
GUWAHATI -781013

This is to certify that the project report entitled "Manufacture of Ethanol from Ethylene "submitted by

Astha Kalita (Class Roll No: 19/295)
Diviya Jyoti Basumatary (Class Roll No: 19/280)Jimi
Hazarika (Class Roll No: 19/270)
Pranjit Boro (Class Roll No: 19/393)

is a bonafide research work which is being carried out under my guidance and supervisions for the award of the degree of "Bachelor of Technology" in Chemical Engineering. This is to certify that the study is the result of their own investigations and the thesis, as a whole or part of it, has not been submitted for the award of any degree elsewhere.

Sarma
30/6/2023

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DECLARATION FROM THE AUTHORS

We sincerely declare that:

1. The manuscript is not an exact copy from any source.
2. The information presented in this work are correct to the best of knowledge of the authors.
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We pay our respect and love to our parents and all other family members and friends for their love and encouragement throughout our career.

ABSTRACT

The world ethanol production has recently seen an incremental growth mainly due to economic and environmental security concerns, worldwide. Ethanol has good burning characteristics and may be considered as attractive transportation fuel alternates. An analysis of the synthetic ethanol production via direct hydration process is presented in this study. Since 1947, synthetic ethanol has been produced via direct hydration of ethylene replacing the indirect hydration of ethylene. The development of the process model is crucial as it involves with rigorous non-linear or complex equations for its sustainable future growth. In order to gain better yield, product quality as well as flexibility and lower energy consumption of the reactor used for the ethanol production, there is a great interest to develop an effective model based control system for the process. Developing the effective control strategy is the major challenge so as to construct a suitable model which employs the dynamics of the process. In this study, an overview of the ethanol production via direct hydration of ethylene is carried out in order to give in-depth understandings on the complexity of its process dynamics and possible strategies ahead to overcome the problems.

PROJECT AT A GLANCE

The plant capacity is 8250 tons producing Ethanol per year. Some of the major process equipment used in the setup is- catalytic fixed bed reactor, heat exchanger, scrubber for the separation of gases from gaseous mixtures of non-condensable gases by transfer into a liquid solvent, and distillation column. This project requires the theoretical and practical application of the key concepts of mass transfer, heat transfer, fluid dynamics and process equipment design.

The basis of the operation for the project is taken 100 kmol/hr combined feed for the material balance of the plant and 1 hr for the energy balance operations.

The aim of the present work is to reach 60 % coversion of ethylene using phosphoric acid as a catalyst on the bed of diatomiceous earth.

The utilities used are water, steam, catalysts (H_3PO_4), reboiler, condenser and cooling jacket. The total amount of water used in various operation is 91327.40 kg (water utility)

Amount of steam required = 30211.5631 kg (steam utility)

Reboiler duty = 68278132.79 KJ

Condenser duty=60874432.59 KJ

Reaction inside the reactor is exothermic.

1-2 Heat exchanger-

Area of HE = 297.48 > 200 ft^2 shell and tube HE Uc & Ud are 42.51 and 40 Btu/hr ft F

Rd=0.00147

Pressure drop in shell side=0.098 psi < 2 psi Pressure drop in tube side 7.99 psi < 10 psi

Storage tank-

Tank volume 10977.676 m^3

Height 13.079 m

Diameter = 32.694 m

Standard thickness of the tank = 6 mm

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CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION AND PROPERTIES:

Ethanol, also known as ethyl alcohol or grain alcohol, is a chemical compound with the molecular formula C_2H_5OH. It is a colorless, volatile liquid with a characteristic odor and a flammable nature. Here are some important chemical properties of ethanol:

a. Molecular Weight: The molecular weight of ethanol is approximately 46.07 g/mol.

b. Solubility: Ethanol is highly soluble in water, as well as in many organic solvents. It forms a homogenous mixture when mixed with water, and this property makes it useful as a solvent in various applications.

c. Boiling Point: The boiling point of ethanol is 78.37°C (173.1°F). It has a relatively low boiling point, which allows it to evaporate easily.

d. Density: The density of ethanol is about 0.789 g/cm^3 at 20°C (68°F). It is less dense than water, which means that ethanol floats on water.

e. Miscibility: Ethanol is miscible with a wide range of organic solvents, such as acetone, benzene, chloroform, and diethyl ether. It is also miscible with many polar and non-polar compounds.

f. Acidity: Ethanol is a weak acid. In aqueous solutions, it can undergo a partial ionization to form ethoxide ions ($C_2H_5O^-$) and hydrogen ions (H+). However, the acidity of ethanol is relatively low.

g. Flammability: Ethanol is highly flammable, and its vapor can form explosive mixtures with air. The flash point (the temperature at which it can ignite) of ethanol is about 13°C (55°F). Special precautions should be taken when handling and storing ethanol to prevent fire hazards.

h. Oxidation: Ethanol can be oxidized to acetaldehyde (CH_3CHO) and further to acetic acid (CH_3COOH) under certain conditions. This property is utilized in the production of vinegar through fermentation and oxidation processes.

i. Reactivity: Ethanol can undergo various chemical reactions, including esterification, dehydration, halogenation, and reduction, depending on the conditions and reactants involved. It is a versatile compound used in organic synthesis and industrial processes.

j. Toxicity: Ethanol is a psychoactive substance and can cause intoxication when consumed in excessive amounts. Prolonged and excessive alcohol consumption can lead to various health issues, including liver damage, cardiovascular problems, and neurological disorders.

These are some of the key chemical properties of ethanol. Its versatile nature and properties make it valuable in numerous applications, such as in the production of alcoholic beverages, fuel, solvents, pharmaceuticals, and personal care products.

1.2 APPLICATION:

Ethanol is a widely used biofuel produced through the fermentation of sugars or biomass feedstock. India, along with many other countries, has been actively promoting ethanol production as an alternative to fossil fuels. Here is some information about ethanol manufacturing plants in India and abroad. Ethanol has several commercial uses across various industries. Here are some of the major applications of ethanol:

a. Fuel Additive: Ethanol is commonly used as a fuel additive in gasoline, particularly in blends such as E10 (10% ethanol and 90% gasoline) and E85 (85% ethanol and 15% gasoline). Adding ethanol to gasoline helps increase octane ratings, improve combustion efficiency, reduce emissions, and decrease dependence on fossil fuels.

b. Biofuel: Ethanol is a renewable biofuel derived from plant materials, primarily corn, sugarcane, or cellulosic feedstock. It is used as a substitute for gasoline in vehicles that can run on ethanol or flex-fuel vehicles (FFVs). Ethanol can be blended with gasoline in different ratios, offering an environmentally friendly alternative to traditional fossil fuels.

c. Alcoholic Beverages: Ethanol is the primary component responsible for the intoxicating effects in alcoholic beverages. It is produced through the fermentation of sugars by yeast. Various types of alcoholic drinks, such as beer, wine, and spirits, are made using different fermentation and distillation processes involving ethanol.

d. Industrial Solvent: Ethanol is a versatile solvent used in a wide range of industries, including pharmaceuticals, cosmetics, personal care products, paints, inks, and cleaning products. It acts as a solvent to dissolve and extract substances, as well as a carrier for active ingredients.

e. Chemical Intermediates: Ethanol serves as a raw material or intermediate in the production of various chemicals. It is used in the manufacturing of ethyl acetate, ethylene, acetic acid, ethylamines, and other organic compounds.

f. Disinfectants and Sanitizers: Ethanol's antiseptic properties make it a key ingredient in hand sanitizers, surface disinfectants, and antiseptic solutions. Its ability to kill bacteria and viruses has made it a crucial component in maintaining hygiene and preventing the spread of diseases.

g. Laboratory and Medical Applications: Ethanol is widely used in laboratories as a solvent for various analytical techniques, such as chromatography. It is also used for tissue preservation and in the production of medicines, vaccines, and medical devices.

CHAPTER 2

LITERATURE REVIEW

From the research paper "Ethanol Production via Direct Hydration of Ethylene: A review Nur Syaera Hidzir1,a , Ayub Md Som2,b and Zalizawati Abdullah3,c 1,2,3Faculty of Chemical Engineering, Universiti Teknologi Mara, 40450 Shah Alam, Selangor, Malaysia a syaera88@gmail.com, b ayub522@salam.uitm.edu.my, c zalizawati8653@salam.uitm.edu.my" we have studied the production of ethanol from ethylene via direct hydration.

2.1 Introduction:

Ethanol is a liquid substance that is volatile, colorless and has a slight odor. It apparently burns with smokeless blue flames that are not always visible in normal light. It presents widely in nature and has many applications in the industrial and pharmaceutical sectors as a solvent of substances intended for human contact consumption, including scents, flavorings, colorings, and medicines. Ethanol is also used with mixed gasoline and in 100% ethanol fueled vehicles . Ethanol production had an extreme requirement globally as a fuel additive as 1.02 × 1011 liters were produced in 2010. Most of the ethanol produced is used as motor fuel or an additive in gasoline to improve its octane level. As a liquid fuel, ethanol has long-term advantages. The increase in the world ethanol production is mainly due to the economic and environmental security concern, worldwide. At certain countries like Europe, India, China, and Brazil, the ethanol production is aimed for reducing petroleum import and increasing the consumption and production of renewable fuel. There are several ways to produce ethanol production such as fermentation of ethanol, indirect hydration (esterification-hydrolysis) process and direct hydration of ethylene . Ethanol is produced by petrochemical through direct and indirect hydration as well as via biological processes by fermenting sugars with yeast . Most of the industrial processes were done by fermentation process but the output was not reliable.

2.2 Ethanol Production by Direct Hydration of Ethylene:

Synthetic ethanol which is produced by hydration of ethylene has the purity of 95-96%, this method is followed by all modern industries having a yield about 95-97% of ethanol, this is a catalytic gaseous reaction where approximately about 5-6 kg of phosphoric acid is used. Commonly kieselguhr or diatomaceous earth is selected as support for phosphoric acid deposition on their surface.

Ethylene and water are pumped from the spheres and storage tanks respectively to the stream of the recycling pipe line which is fed to the effluent pre heater shell side and then it heated to 300°C in furnace which is uses off gas as fuel along with natural gas, the pressure about 6.8 MPa is maintained by the feed pumps which is controlled by the reactor outlet control valve, reactor is packed bed and converts reactant to product with a conversion of 4-25% and a side reaction will produce byproduct acetaldehyde which is sold or hydrogenated to produced ethanol. Main reaction:

$$CH_2{=}CH_2 + H_2O \xrightarrow[\text{Conversion } 60\%]{H_3PO_4,\ 300^\circ C,\ 6.8MPa} C_2H_5OH$$

The outlet vapour mixture of the reactor is separated into products and unreacted reactants in the high- pressure separator, before passing through effluent preheater tube side which is used to heat the feed mixture as the reaction is exothermic one mole of ethylene and water will produce 45.6KJ of energy after complete conversion into ethanol. Unreacted reactants present in the separator top outlet are scrubbed with water to dissolve the ethanol carry over into the recycle stream. The vapours are recycled having 80-85% concentration of ethylene in such way so that the molar ratio of water to ethylene is 0.6:1 is maintained. The bottom of separator and scrubber is fed to Hydrogenator to convert acetaldehyde to ethanol on the nickel packed catalyst by adding hydrogen to acetaldehyde.

Side reaction:

$$C_2H_2 + H_2O \longrightarrow CH_3CHO$$

Reacted vapour is fed to acetaldehyde reduction column to separate Unreacted acetaldehyde and recycle to the reactor are some part can be sold as by-product based on market demand, the bottom stream is fed to light and heavy (purifier) column to distil out ethanol and increase it concentration.

REACTIONS:

$$\begin{aligned} C_2H_4 + H_2O &\longrightarrow C_2H_5OH \\ C_2H_2 + H_2O &\longrightarrow CH_3CHO \\ C_2H_5OH &\longrightarrow \tfrac{1}{2}(C_2H_5)_2O + \tfrac{1}{2}H_2O \end{aligned}$$

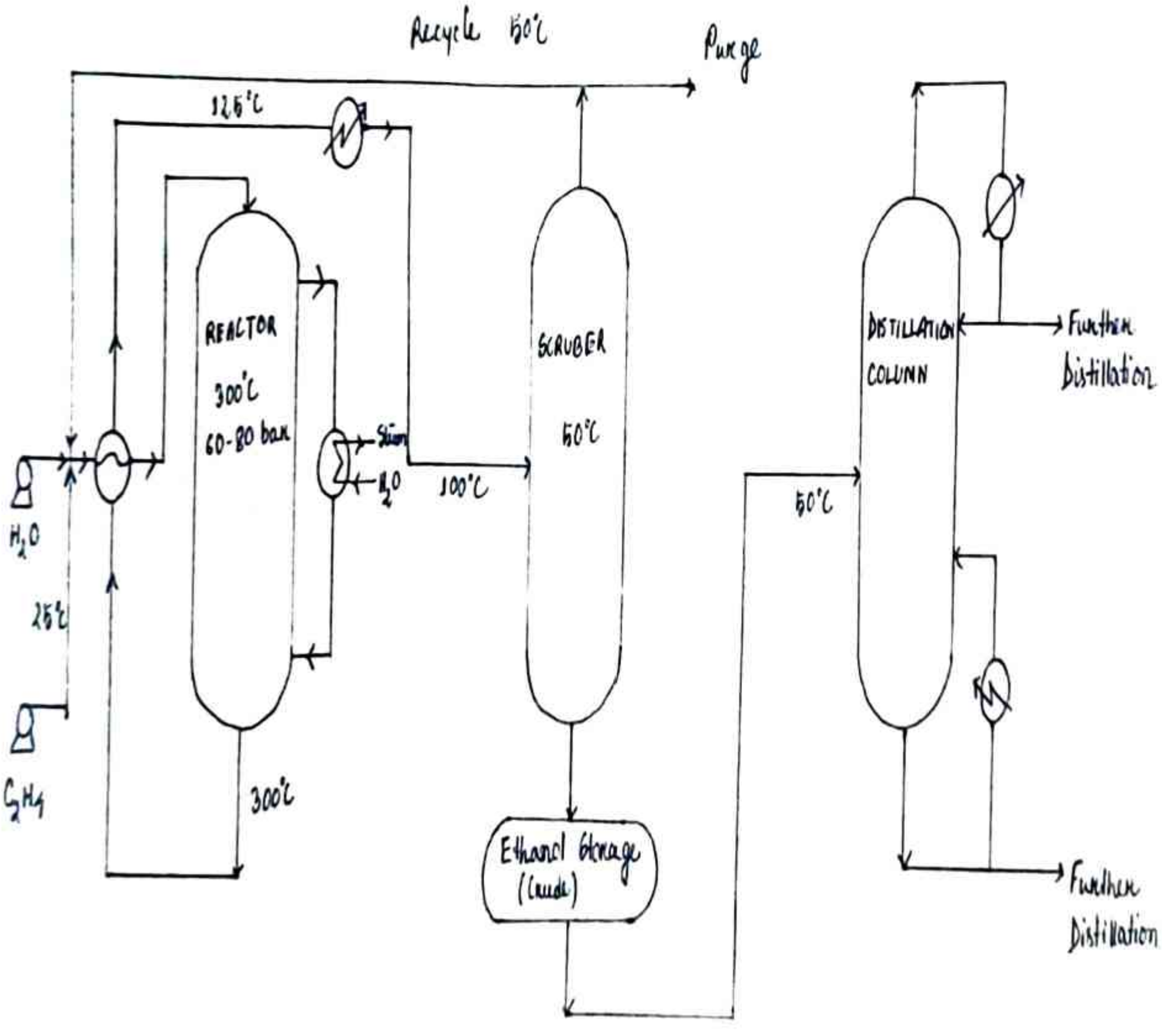

Fig. 2.1 Flow sheet to form ethanol from ethylene

2.3 Catalyst Used In the Process:

The direct hydration of the ethylene has been carried out since about 60 years ago in the chemical industry over catalyst consisting of the silica gel with a high loading of phosphoric acid. Catalyst is characterised as the supported liquid phase and the catalytic active bound on a carrier as the concentrated liquid acid. Phosphoric acid on silica gel is more resistant to leaching than the acid on metal phosphate. The Silica gel-supported phosphoric acid catalyst (H_3PO_4/SiO_2) is used in the industry as it has high selectivity in excess ethylene. The ethanol production rate increases remarkably with increasing phosphoric acid loadings. Phosphoric acid present in liquid like form on silica gel has a pure acidic nature. The higher condensed phosphates take longer time to be hydrolysed. The amount of the catalyst phosphoric acid was described by Cavani et. al. There have been several researches on the hydration of ethylene over different metal phosphates (metal: Ge, Zr, Ti and Sn) and phosphoric acid impregnated metal phosphates at high pressure. These catalyst effects were compared with phosphoric acid on silica and the result showed that the conversions were slightly higher by using the impregnated metal phosphates.

2.4 Reactor Used For the Process:

Fixed bed reactor is a reactor in which a stationary solid catalyst is used to carry out reactions whereby the reactant is in mobile fluid phase that takes place on the surface of the catalyst. The reactant diffuses, adsorbs and reacts on the active surface of the catalyst. Catalytic fixed bed reactors are the most widely used reactor for gas phase reactants as well as in the production and synthesis of large scale basics chemicals and intermediates.
feedstocks.

2.5 Process Selection

Out of the process of indirect and direct catalytic hydration for the production of ethanol from ethylene we have selected the direct hydration one.
This is because in case of the indirect catalytic hydration of ethylene process, it has several disadvantages such as

i The large volume of dilute sulphuric acid to handle,
ii The energy required for its concentration and
iii Corrosion caused by the acid which are not seen in case of direct hydration.

The advantages of direct catalytic hydration process are:

i Higher conversion than indirect catalytic hydration process (up to 97 %)
ii As conversion is higher, unreacted compounds are formed very less and thus purification steps become simpler.
iii Recycle stream is there which passes a part of the recycled gas to the ethylene purification section to remove impurities and inhibit their buildup.

Around 20% of world ethyl alcohol capacity is synthetic, most being produce from catalytic direct hydration process.
Comparing the properties of the catalyst in both the processes

PROPERTIES	MOLYBDENUM OXIDE	SILVER OXIDE
Ethanol Conversion	97%	92%
Shelf Life	Indefinite if stored properly	24 months
Regeneration	Convenient	Combustion based

Table 2.1: Properties of Catalyst

PROPERTIES	PROCESS 1 (DIRECT HYDRATION)	PROCESS 2 (INDIRECT HYDRATION)
RAW MATERIALS	ETHYLENE	ETHYLENE
BY PRODUCT	DIETHYL ETHER	DETHYL ETHER
YIELD	97%	92%
CATALYST & ACIDS	PHOSPHORIC ACID	SULPHURIC ACID
TEMPERATURE & PRESSURE	(230-300°C)& (60-80 bar)	(65-80°C) &(10-30 bar)

Table 2.2 Comparison of Processes

CHAPTER 3

MATERIAL BALANCE

Definitions of All Abbreviations Used In Our Calculations:

C_2H_5OH: Ethanol

C_2H_4: Ethylene

C_2H_2: Acetylene

CH_3CHO: Acedaldehyde

$(C_2H_5)_2O$: Diethylether

Basis: 100 Kmol/hr combined feed (Recycle+Fresh)

Composition of ethylene: 99.9% Ethylene

0.1 % Acetylene

3.1 Reactor Material Balance

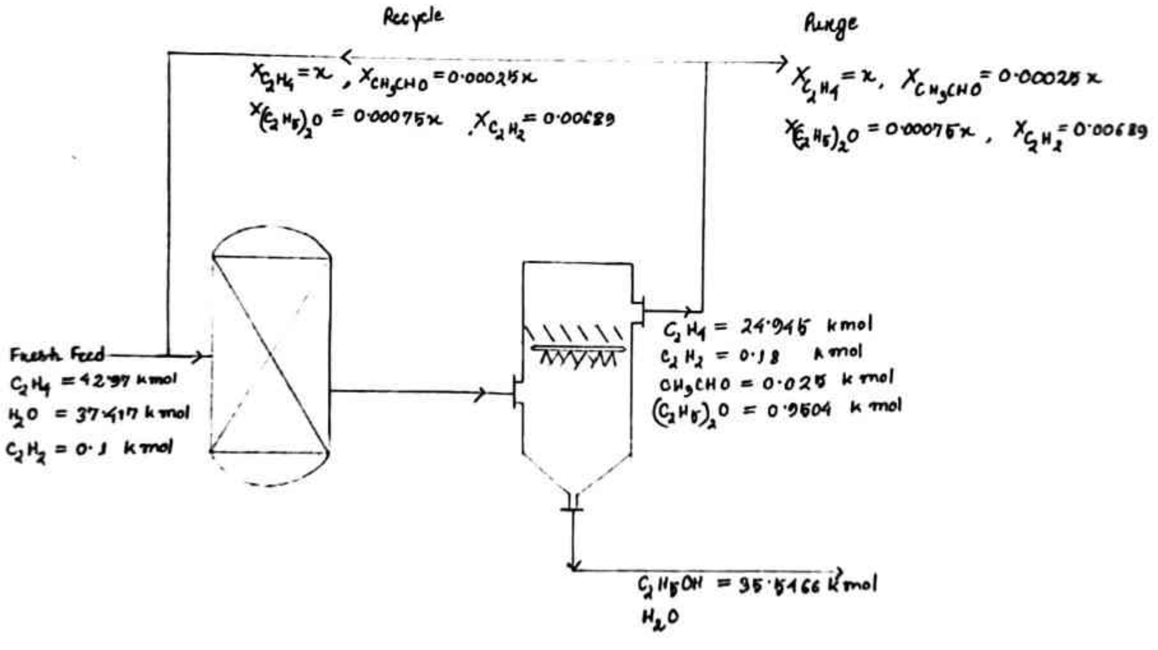

Fig. 3.1 Reactor Balance Diagram

In the reactor following reactions are taking place:

a. $C_2H_4 + H2O \longrightarrow C_2H_5OH$ $\Delta H = - 45$ Kj/mol
b. $C_2H_2 + H_2O \longrightarrow CH_3CHO$ $\Delta H = - 151.324$ Kj/mol
c. $C_2H_3OH \longrightarrow 1/2\ (C_2H_5)_2O + 1/2H_2O$ $\Delta H = 30.367$ Kj/kmol

Composition of Feed:

C_2H_4: H_2O =1:0.6

C_2H_2 = 0.2% of 100 kmol/hr

CH_3CHO = 0.005% of 100 kmol/hr

$(C_2H_5)_2O$ = 0.015% of 100 kmol/hr

∴ C_2H_4 & H_2O is 99.78 % of 100 kmol/hr in 1: 0.6 ratio

In Feed Composition to the Reactor:

C_2H_4 = 1/1.6 x 99.78 = 62.3625 kmol/hr

H_2O = 0.6/1.6 x 99.78 = 37.417 kmol/hr

C_2H_2 = 0.2 kmol/hr

CH_3CHO = 0.005 kmol/hr

$(C_2H_5)_2O$ = 0.015 kmol/hr

In The Reactor Following Reactions Are Taking Place:

$$C_2H_4 + H_2O \xrightarrow[\text{Conversion 60\% (assumed)}]{H_3PO_4} C_2H_5OH \longrightarrow (1)$$

$$C_2H_2 + H_2O \xrightarrow[\text{Conversion 10\% (assumed)}]{} CH_3CHO \longrightarrow (2)$$

$$C_2H_5OH \xrightarrow[\text{Conversion 5\% (assumed)}]{} ½\,(C_2H_5)_2O + ½(H_2O) \longrightarrow (3)$$

For reaction (1)-

C_2H_5OH formed = 0.60* 62.3625 = 37.4175 kmol/hr

H_2O reacted = 37.4175 kmol/hr

C_2H_4 unreacted = 0.40*62.3625 = 24.945 kmol/hr

For reaction (2) –

CH_3CHO formed = 0.10 * 0.2= 0.02 kmol/hr

H_2O reacted = 0.02 kmol/hr

C_2H_2 unreacted = 0.90*0.2 = 0.18 kmol/hr

For reaction (3) –

$(C_2H_5)_2O$ formed = ½ *0.05*37.4175 = 0.9354 kmol/hr

H_2O formed = 0.9354 kmol/hr

C_2H_5OH remain in the reactor = 0.95*37.4175 = 35.5466 kmol/hr

Moles of H_2O remain in the reactor = 37.4175+0.9354-37.4175-0.02 = 0.9154 kmol/hr

Moles of CH_3CHO in the reactor = 0.005 + 0.02 = 0.025 kmol/hr

Moles of $(C_2H_5)_2O$ in the reactor = 0.015+0.9354 = 0.9504 kmol/hr

Components	MW gm	Input		Output	
		Kmol/hr	Kg/hr	Kmol/hr	Kg/hr
C_2H_5OH	46.07	-	-	35.5466	1637.6318
C_2H_4	28.05	62.3625	1749.2681	24.945	699.7072
H_2O	18	37.4175	673.515	0.9154	16.4772
C_2H_2	26.04	0.2	5.208	0.18	4.6872
CH_3CHO	44.05	0.005	0.22025	0.025	1.10125
$(C_2H_5)_2O$	74.12	0.015	1.1118	0.9504	70.4436
Total			2430.0		2430.0

Table 3.1 Material balance over reactor

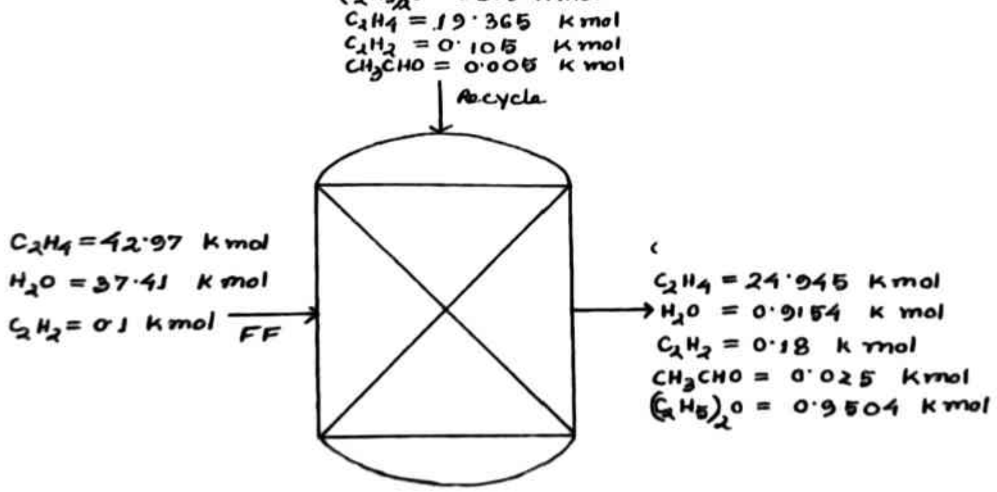

Fig. 3.2 Reactor

3.2 Scrubber Material Balance

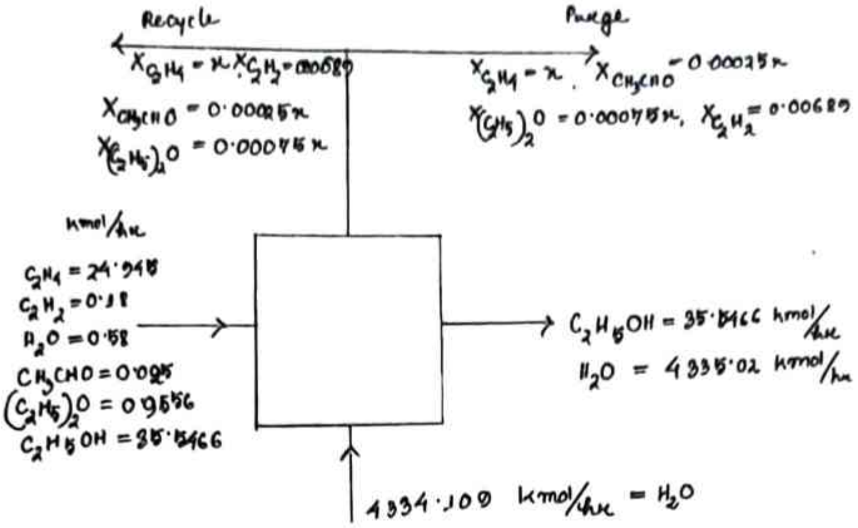

Fig. 3.3 Scrubber

$n = C_2H_4 + C_2H_2 + CH_3CHO + (C_2H_5)_2O$

$= 24.945 + 0.18 + 0.025 + 0.9504$

$= 26.1004$ kmol/hr

Assuming

- i Recycle and purge ratio is 3:1
- ii Fresh feed contain 0.1 kmol/hr CH

$\therefore$ Recycle $= \frac{3}{4} * 26.1004 = 19.5753$ kmol/hr

Purge $= 6.5251$ kmol/hr

Let $X(C_2H_4)x$, $X(CH_3CHO) = 0.00025x$, $X(C_2H_5)_2O = 0.00075x$ & 0.00689 C_2H_2 in both recycle and Purge.

$$x + 0.00025x + 0.00075x + 0.00689 = 1$$

$\Rightarrow$ $1.001x = 0.99311$

$\Rightarrow$ $x = 0.9921$

In recycle and purge

$X(C_2H_4)$ = 0.9921

$X(CH_3CHO)$ = 0.000248

$X(C_2H_5)_2O$ = 0.000744

$X(C_2H_2)$ = 0.00689

∴ C_2H_4 in the recycle = 19.365 kmol/hr

CH_3CHO in the recycle = 0.0049 kmol/hr

$(C_2H_5)_2O$ in the recycle = 0.015 kmol/hr

C_2H_2 in the recycle = 0.105 kmol/hr

C_2H_4 in the purge = 5.64 kmol/hr

C_2H_2 in the purge = 0.075 kmol/hr

CH_3CHO in the purge = 0.0199kmol/hr

$(C_2H_5)_2O$ in the purge = 0.9354 kmol/hr

Recycle (Kmol/hr)		Purge (Kmol/hr)	
Components	Kmol/hr	Components	Kmol/hr
C_2H_4	19.365	C_2H_4	5.64
C_2H_2	0.105	C_2H_2	0.075
CH_3CHO	0.005	CH_3CHO	0.0199
$(C_2H_5)_2O$	0.015	$(C_2H_5)_2O$	0.9354

Table 3.2. Recycle and Purge Compositions

Component	Kmol/hr
C_2H_4	42.9719
H_2O	37.4175
C_2H_2	0.1

Table 3.3 Fresh feed

Enthalpy of output of reactor at 100 °C

H = (1637.6318 * 6966.1147) + (699.70112 * 100 * 1.84184) + (100 * 1.88387 * 4.6872) + (100 * 1.92556 * 16.4772) + (1.10125 * 5837.2044) + (70.4436 *12461.89910)

H = 12425149.7543094 KJ

Enthalpy of stream at 50°C

H = (1637.6318 * 3307.5462) + (699.70112 * 50 * 1.632) + (50 * 1.77 * 4.6872) + (50 * 4.184 * 16.4772) + (1.10125 * 2798.8717) + (70.4436 * 5910.317)

H = 5896940.554024 KJ

ΔH = Enthalpy of stream at 100 °C - Enthalpy of stream at 50°C

= 6528209.2 KJ

Enthalpy of water input = ΔH

$$(MC_p dT)H_2O = 6528209.2$$
$$\Rightarrow M * 4.184 * 20 = 6528209.2$$
$$\Rightarrow M = 78013.972 \text{ Kg / hr}$$
$$\Rightarrow M = 4334.109 \text{ K mol / hr}$$

Therefore total water enter into the scrubber = 4334.109 + 0.9154 = 4335.024 kmol/hr

Component	Input Kmol/hr	Input Kg/hr	Output Kmol/hr	Output Kg/hr
Ethanol	35.5466	1637.6318	35.5466	1637.6318
Ethylene	24. 945	699.707	24.945	699.707
Water	4335.024	78030.432	4335.024	78030.432
Acetylene	0.18	4.6872	0.18	4.6872
Acidaldehyde	0.025	1.10125	0.025	1.10125
Diethylether	0.9504	70.4436	0.9504	70.4436
Total		51162.380		51162.380

Table 3.4 Material balance over the scrubber

3.3 Distillation Column Material Balance

Assuming Efficiency of 60% for distillation column.

Moles of C_2H_5OH in top product = 35.5466*0.60 kmol/hr

=21.327 kmol/hr

Moles of C_2H_5OH in bottom product = 35.5466 * 0.40 kmol/ hr

= 14.218 kmol/ hr

Moles of H_2O in top product = 0.40 * 4334.109 kmol/ hr

= 1733.6436 kmol/ hr

Moles of H_2O in bottom product = 0.60 * 4334.109 kmol/hr

= 2600.46 kmol/ hr

Distillation Column –

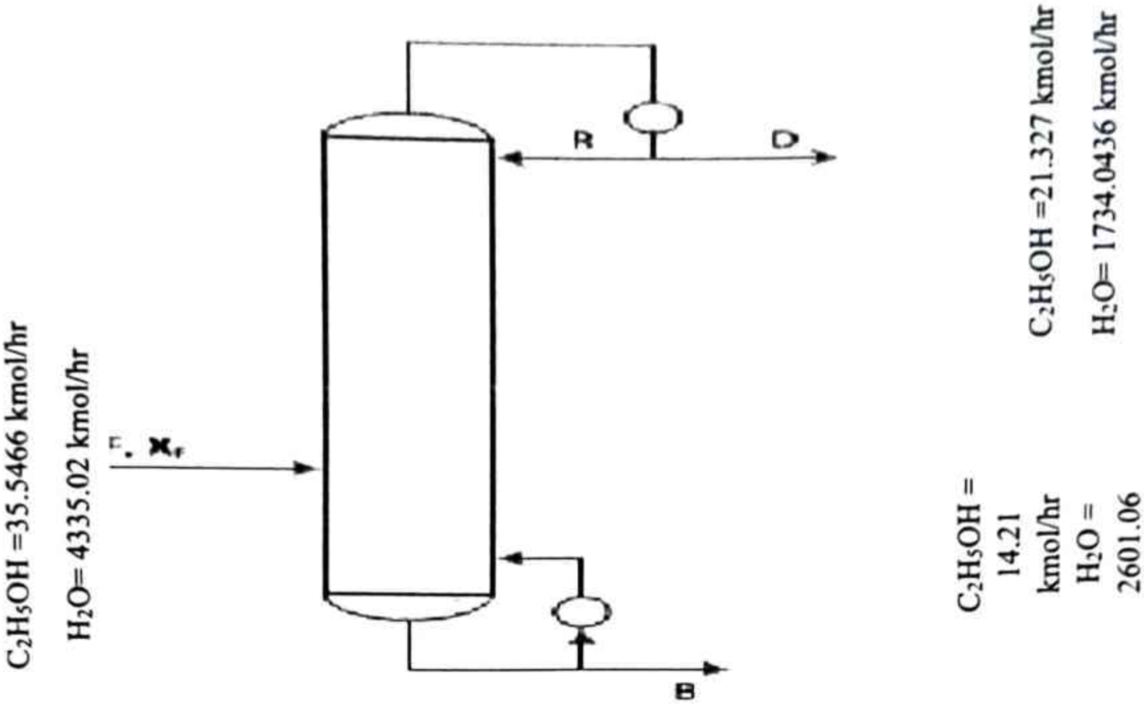

Fig. 3.4 Distillation Column

Components	Input		Output	
	Kmol/hr	Kg/hr	Kmol/hr	Kg/hr
C_2H_5OH	35.5466	1637.6318	35.5466	1637.6318
H_2O	4335.024	78030.4392	4335.024	78030.4392
Total		79668.071		79668.071

Table 3.5 Material balance over distillation column.

3.4 Overall Material Balance

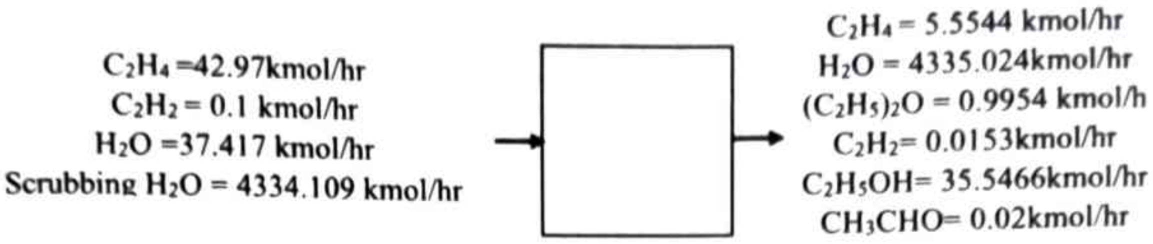

Fig. 3.5 Overall Balance

Components	Input		Output	
	Kmol/hr	Kg/hr	Kmol/hr	Kg/hr
C_2H_5OH	-	-	35.5466	1637.6318
C_2H_4	42.97	1205.30	5.5544	155.80
H_2O	37.4275	673.51	4335.024	78030.652
C_2H_2	0.1	2.604	0.0153	0.3984
CH_3CHO	-	-	0.02	0.881
$(C_2H_5)_2O$	-	-	0.9354	69.3318
Scrubbing H_2O	4334.109	78013.962		
Total		79895.376	-	79895.376

Table 3.6 Overall Material Balance

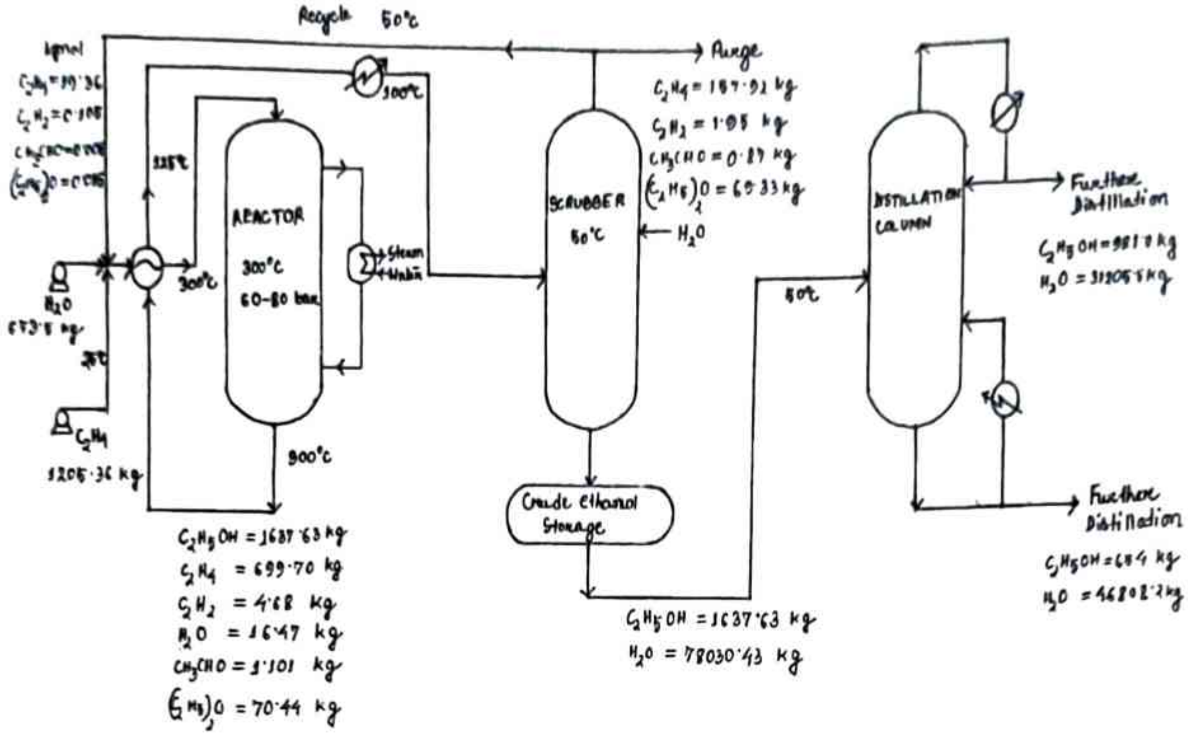

Fig. 3.6 Material Balance Flowchart

CHAPTER 4

MODIFIED MATERIAL BALANCE

Plant capacity assumed to be 8250 tons / annum

= (8250 * 1000)/(Working days) (kg/days)

Let working days = 330

= (8250 * 1000)/(330 * 24) (kg/hr)

= 1041.6667 kg/hr

= 1041.6667/46.07 kmol/hr

= 22.610 kmol/hr

1Kmol feed gives = 35.5466 Kmol/hr ethanol

1Kmol/hr ethanol = (100/35.5466) Kmol feed

22.160 Kmol/hr ethanol = (100 * 22.610)/35.5466 Kmol feed

= 63.6081 Kmol/hr feed

M.F is 22.610/35.546 = 0.6360

2430 kg/hr feed gives = 1637.6318 kg/hr C_2H_5OH

1kg/hr C_2H_5OH = 2430/1637.6318 feed

1041.6667 kg/hr C_2H_5OH = (2430 * 1041.6667)/1637.6318

M.F = 1041.6667/1637.6318

= 0.6360

So, the scale up factor is 0.6360

	Input			Output		
Components	Kmol/hr	Kg/hr	Scale up	Kmol/hr	Kg/hr	Scale up
C_2H_5OH	-	-	-	35.5466	1637.6318	1041.5338
C_2H_4	62.3625	1749.2681	1112.5345	24.945	699.7072	445.0137
H_2O	37.4175	673.515	428.3555	0.9154	16.4772	10.4794
C_2H_2	0.2	5.208	4.371	0.18	4.6872	2.981
CH_3CHO	0.005	0.22025	0.14	0.025	1.10125	0.7004
$(C_2H_5)_2O$	0.015	1.1118	0.7071	0.9504	70.4436	44.8021
Total		2430			2430.0	

Table 4.1 Reactor

	Input			Output		
Components	Kmol/hr	Kg/hr	Scale up	Kmol/hr	Kg/hr	Scale up
C_2H_5OH	35.5466	1637.6318	1041.5338	35.5466	1637.6318	1041.533
C_2H_4	24.945	24.945	445.0137	24.945	24.945	445.0137
H_2O	4335.02	78030.43	49627.35	4335.02	78030.43	49627.35
C_2H_2	0.18	4.6872	2.9810	0.18	4.6872	2.981
CH_3CHO	0.025	1.10125	0.7004	0.025	1.10125	0.7004
$(C_2H_5)_2O$	0.9504	70.4436	44.8021	0.9504	70.4436	44.8021
Total		51162.380			51162.380	

Table 4.2 Scrubber

	Input			Output		
Components	Kmol/hr	Kg/hr	Scale up	Kmol/hr	Kg/hr	Scale up
C_2H_5OH	35.5466	1637.6318	1041.533	35.5466	1637.6318	1041.533
H_2O	4335.02	78030.43	49627.35	4335.02	78030.43	49627.35
Total		79668.061			79668.061	

Table 4.3 Distillation Column

Components	Input			Output		
	Kmol/hr	Kg/hr	Scale up	Kmol/hr	Kg/hr	Scale up
C_2H_5OH	-	-	-	35.5466	1637.6318	1041.533
C_2H_4	42.97	1205.30	766.5708	5.5544	155.800	99.08
H_2O	37.4175	673.51	428.3523	4335.02	78030.43	49627.35
C_2H_2	0.1	2.604	1.6561	0.0153	0.39841	0.2534
CH_3CHO	-	-	-	0.02	0.881	0.5603
$(C_2H_5)_2O$	-	-	-	0.9354	69.3318	44.0950
Scrubbing H_2O	4334.109	78013.962	49616.879	-	-	-
Total		79895.076			79895.076	

Table 4.4 Overall Balance

CHAPTER 5

ENERGY BALANCE

Basis: 1 hr operation

Reference Temperature: 25°C

All limit are in Kelvin

5.1 Energy Balance Calculations for Feed

Energy of the recycle stream at 50°C

$$H = \int_{273}^{323} mCpdT_{C_2H_4} + \int_{273}^{323} mCpdT_{C_2H_2} + \int_{273}^{323} mCpdT_{CH_3CHO} + \int_{273}^{323} mCpdT_{(C_2H_5)_2O}$$

$$= [345.9244 * 1.632(323 - 298)] + [2.7276 * 1.779 *(323 - 298)]$$

$$+0.1400\int_{273}^{323}$$

$$[34.140 + 0.040020T + (1.5634 * 10^{-4}T^2) - (1.6445*10^{-7}\,T^3) + (4.7248*10^{-11}\,T^4)]dT$$

$$+0.7071\int_{273}^{323}$$

$$[35.979 + 0.28444T - (1.2673*10^{-6}T^2) - (1.0128*10^{-7}T^3) + (3.4529*10^{-11}T^4)]dT$$

$$= 14113.7155+121.31001+234.511+2147.1190$$

$$= 16616.65551 \text{ KJ}$$

Energy of the fresh stream at 25°C

$$H = \int_{273}^{298} mCpdT_{C_2H_4} + \int_{273}^{298} mCpdT_{C_2H_2} + \int_{273}^{298} mCpdT_{H_2O}$$

$$= (766.570 * 1.548 * 25) + (1.6561 *1.737 * 25) + (428.3523*1.864*25)$$

$$= 29666.28996 + 71.9161 + 44827.0682$$

$$= 74565.27426 \text{ KJ}$$

Total energy of the feed stream = 91181.92977 KJ

5.2 Energy Balance Calculations for Heat Exchanger

Input energy of Feed Stream at HE= Total energy of feed stream

$$\Delta H_{in} = 91181.92977$$

Output temperature of feed stream at HE = 300°C

C_P of all the component at 300°C

C_2H_4 = 1.535 kJ/kgK

H_2O = 1.864 kJ/kgK

C_2H_2 = 2.3344 kJ/kgK

C_2H_5OH = 0.745 Btu /lb°F

= 3.11857 kJ/kgK

$CH_3CHO = 34.140 + (0.040020 * T) + (1.5634 * 10^{-4}\ T^2) - (1.6445 * 10^{-7}\ T^3) + (4.7248 * 10^{-11}\ T^4)$

$(C_2H_5)_2O = 35.979 + (0.28444 * T) - (1.2673 * 10^{-6}\ T^2) - (1.0128 * 10^{-7}\ T^3 + (3.4529 * 10^{-11}\ T^4)$

Output energy of feed stream at H.E

$$\Delta H_{out} = \int_{273}^{573} mCpdT_{C_2H_4} + \int_{273}^{573} mCpdT_{C_2H_2} + \int_{273}^{573} mCpdT_{CH_3CHO} + \int_{273}^{573} mCpdT_{(C_2H_5)_2O} + \int_{273}^{573} mCpdT_{H_2O}$$

$$= [1112.5345 * 1.535 * 300] + [3.3122 * 300 * 2.3344] + [0.1400 * 20430.234] + [44645.499 * 0.7071] + [428.3555 * 300 * 1.864]$$

$$= 512322.1373 + 2319.599 + 239536.39 + 2860.23276 + 312568.83234$$

$$= 788607.1914 \text{ KJ}$$

$\therefore \Delta H_{out}$ = 788607.1914 KJ

$\therefore \Delta H_{out} - \Delta H_{in} = 788607.1914 - 91181.929 = 697425.2616$ KJ

Input energy of product stream at HE = Total output Energy of Reactor output

= 2840965.63 KJ

Energy balance at Heat Exchanger

Input energy of the product stream at heat exchanger - Energy lost by the product

= Output energy of the product stream at HE

Energy lost by the product = $\Delta H_{out} - \Delta H_{in}$ in H.E

= 697425.2616 KJ

$\therefore$ Output energy of product stream at H.E = 2840965.276KJ - 697425.2616 KJ

= 2143540.014 KJ

$\Delta H = \sum mCpdT_{\text{all components}}$

= 2143540.014 K

= [1041.533 * 3.11857 * (573 - T)] + [1.535 * (573 – T) * 445.0137] + [10.4794 * 1.864 * 9 (573 - T)] + [2.9810 * 2.009 * (573 - T)] + [0.7004 * (573 -T) * 82.55735] + [44.8021 * (573 - T) * 183.19227]

= 2143540.014 K

= (573 - T)[3248.093568 + 683.0960 + 19.5336 + 4.99 + 57.8231 + 8207.3800]

= 2143540.014 K

= 2220.91635(573-T)

= 2143540.014 K

= 573-T

= 175.399287

= 397.600713 K

= 125°C

5.3 Energy Balance Calculations for the Reactor

For reaction

$C_2H_4\,(g) + H_2O\,(g) \xrightarrow{\text{60\% conversion}} C_2H_5OH$

$\Delta H_1 \quad = -\int_{298}^{573} mCpdT_{\text{reactant}}$

= - 966706.795 KJ/hr

$\Delta H^{\circ}_{298} = \sum[Enthalpy\ of\ formation)product] - \sum[Enthalpy\ of\ formation)Reactant$

= - 234.81 – (-241.822 + 52.283)

= - 45000 KJ/kmol

Ethanol formed in the reactor = 37.4175 kmol/hr.

For 1 kmol of ethanol formed = - 45000 kmol/KJ

∴ For 37.4175 kmol of ethanol formed

$\Delta H_2 = \Delta H^{\circ}_{298}$ = - 45000 * 37.4175 KJ/hr

= - 1683787.5 KJ/hr

$\Delta H_3 \quad = \int_{298}^{573} mCpdT\text{product}$

$= \int_{298}^{573}$ [27.091+ 0.10005T + 1.0957*10^{-4} T^2 - (1.5046*10^{-7} T^3)+ (4.6601*10^{-11}

T^4)]dT x 1041.533

= 1096.352* 23390.00016 KJ/hr

= 25643678.3 KJ/hr

$\Delta H_{573} = \Delta H_1 + \Delta H_2 + \Delta H_3$

= 24926597.6 KJ/hr

= 666174.8539 KJ/mol

For reaction

$$C_2H_5OH \xrightarrow[\text{5\% conversion}]{} \tfrac{1}{2}\,(C_2H_5)_2O + \tfrac{1}{2}\ H_2O$$

$\Delta H^{\circ}_{298} = [1/2\ (-25.27) + 1/2\ (-241.826)\ ] - (-277.63)$

= 30367 KJ/kmol

$(C_2H_5)_2O$ & H_2O formed in the reactor = 1.8708 kmol/hr

For 1kmol of $(C_2H_5)_2O$ & H_2O formed $\Delta H298$ = 30367 KJ

For 1.8708 kmol of $(C_2H_5)_2O$ & H_2O

ΔH_{298} = 1.8708 *30367

= 56810.5836 KJ/hr

$\Delta H_1 = \int_{573}^{298} mCpdT$ C_2H_5OH

= 1096.3522 * 1.9164 * (275)

= -577788.5729 KJ/hr

$\Delta H_3 = \int_{298}^{573} mCpdT$ $(C_2H_5)_2O$ + $\int_{298}^{573} mCpdT_{H2O}$

= (10.7084 * 1.864 * 275) + (44.09021* 41839.75)

= 1855904.7842 KJ/hr

$\Delta H_{573} = \Delta H_1 + \Delta H_{298} + \Delta H_3$

= 56810.5236 + 1855904.7842 – 577722.5729

= 1334926.794 KJ/hr

= 713559.33 KJ/kmol

For Reaction

$C_2H_2 + H_2O \xrightarrow{\qquad} CH_3CHO$

$\Delta H_{298} = -166.4 - [226.75 + (-241.826)]$

$= -151.324$ KJ/Kmol

$= -151324$ KJ/Kmol

CH_3CHO formed in the reactor = 0.02 kmol/hr

For 1 kmol of CH_3CHO formed $\Delta H_{298} = -151324$ kJ

For 0.02 kmol of CH_3CHO formed $\Delta H_{298} = -3026.48$ kJ/hr

$= \Delta H_2$

$\Delta H_1 = \int_{573}^{298} mCpdT_{C2H2} + \int_{573}^{298} mCpdT_{H2O}$

$= (3.3122 * (-275)*1.737) + (10.7084* 4.186*(-285))$

$= -13909.1979$ kJ/hr

$\Delta H_3 = \int_{298}^{573} mCpdT_{CH3CHO}$

$= 0.560316*32068.58$

$= 17968.21779$ kJ/hr

$\Delta H_{573} = 1032.5398$ kJ/hr

$= 51626.99427$ kJ/kmol

Heat of reaction at the reactor at 573K = 666174.8539+713559.33+51626.99427

$= 1431361.178$ kJ/kmol

Heat input at the reactor –

$\Delta H_{in} = \Delta H_{out}$ of the Heat Exchanger

$= 788607.19194$ kJ/hr

$= 7886.071914$ kJ/kmol

Heat output at the reactor –

$\Delta H_{out} = \int_{273}^{573} mCpdT_{products}$

$= (1041.5338 * 300 * 3.118)_{C_2H_5OH} + (2.3344 * 300 * 2.9840)_{C_2H_2} + (1.535 * 300 * 445.0237)_{C_2H4} + (10.4794 * 1.864 * 300)_{H_2O} + (0.7004 * 20433.638)_{CH_3CHO} + (44.8021 * 36594.712)_{(C_2H_5)_2O}$

$= 2840965.63$ kJ/hr

$= 45410.11262$ kJ/kmol

Input + Generation = Output+ Q

⇒ 7886.071914 + 143161.178= 45410.11262+ Q

⇒ Q = 1393837.137 kJ/kmol

⇒ Q = 24210198.5 KJ/Hr

Let 'm' be the mass of H_2O that extract Q amount of energy.

$\therefore mC_PdT = Q$

=> $m[C_P(-298+373)+\lambda] = 24210198.5$

=> m = $(24210198.5)/([(75 * 3.76) + 2260])$

=> m = 9524.0749 kg

Input(KJ/Kmol)		Output(KJ/Kmol)	
Input	7886.07191	Output	45410.112
Generation	143161.178		
Q	-1393837.137		
Total	45410.112		

Table 5.1 Energy balance across the reactor

5.4 Energy Balance Calculations for Cooler

Input Energy of the cooler

$= \int_{273}^{398} mCpdT_{C_2H_4} + \int_{273}^{398} mCpdT_{C_2H_2} + \int_{273}^{398} mCpdT_{CH_3CHO} + \int_{273}^{398} mCpdT_{(C_2H_5)_2O} +$
$\int_{273}^{398} mCpdT_{H_2O} + \int_{273}^{398} mCpdT_{C_2H_5OH}$

= (445.0137*125*1.9464)+(2.9810*125*1.967)+(0.7004*7020.223) +(44.8021*15971.850)+ (10.4794*1.925)+ (1041.5338*8926.1022)

= 10128853.34 kJ/hr

Output energy of the cooler

$= \int_{273}^{373} mCpdT_{C_2H_4} + \int_{273}^{373} mCpdT_{C_2H_2} + \int_{273}^{373} mCpdT_{CH_3CHO} + \int_{273}^{373} mCpdT_{(C_2H_5)_2O} +$
$\int_{273}^{373} mCpdT_{H_2O} + \int_{273}^{373} mCpdT_{C_2H_5OH}$

=(445.0137*100*1.84184)+(2.9810*100*1.8837)+(0.7004*5837.2044) +(44.8021*12461.89910)+ (10.4794*100*1.92556)+ (1041.5338*6966.1147)

= 7902395.348 kJ/hr

Now,

$(\text{Input- Output})_{cooler}$ = 2226457.992 kJ/hr

∴ Amount of cooling water needed = $2226457.992/(4.186 * (50 - 10))$

= 13297.04964 kg

5.5 Energy Balance Calculations for the Scrubber

Input of the scrubber = Output of the cooler + $\int_{273}^{303} (mCpdT)$ H_2O

$= 7902395.348 + \int_{273}^{303} (49616.88619 * 4.186) dT$

= 7902395. 348 + 6230888.568 KJ/hr

= 14133283.92 KJ/hr

Output of the scrubber

$= \int_{273}^{323} mCpdT_{C_2H_4} + \int_{273}^{323} mCpdT_{C_2H_2} + \int_{273}^{323} mCpdT_{CH_3CHO} + \int_{273}^{323} mCpdT_{(C_2H_5)_2O} +$

$\int_{273}^{323} mCpdT_{H_2O} + \int_{273}^{323} mCpdT_{C_2H_5OH}$

= (445.0137 * 50 * 1.632) + (2.9810 * 50 * 1.77) + (0.7004 * 3798.8717) + (44.8021 * 5910.3177) +

(49627.36559 * 4.186 * 50) + (1041.5338 * 3307.5462)

= 6230321.75264 KJ/hr

5.6 Energy Balance Calculations for Distillation Column

Feed Temperature = 50°C

Bottom Temperature = 90 °C

Top Temperature = 80°C

Distillate Temperature = 70 °C

Bottom Product Temperature = 95 °C

Bottom product calculations

= $\int_{273}^{368} (416.641 * 3.7464)dT + \int_{273}^{368} (29776.385 * 4.184)dT$

= 148285.865 + 11835517.66

= 11983803.53 kJ/hr

Top product calculations

= $\int_{273}^{343} mCpdT_{C_2H_5OH} + \int_{273}^{343} mCpdT_{H_2O}$

= (624.892 * 3.3906 * 70) + (19846.751 * 70 * 4.186)

= 148313.117+5815494.978 kJ/hr = 5963808.095 KJ/hr

We know

Input + Reboiler duty = Condenser duty + Bottom product +Distillate product

Input of the distillation column

= $\int_{273}^{323} mCpdT_{C_2H_5OH} + \int_{273}^{323} mCpdT_{H_2O}$

= (3.013 * 50 * 1041.5338) + (4.186 * 49627.35 * 50)

= 10543911.42 kJ/hr

Reboiler - Condenser duty = 11983803.53 + 5963808.095 - 10543911.42

= 7403700.205 kJ/hr

Reboiler duty = $\int_{263}^{368} mCpdT_{C_2H_5OH} + \int_{273}^{323} mCpdT_{H_2O} + m\lambda H_2O + m\lambda C_2H_5OH$

= (416.641 * 5 * 3.74647) + (29776.385 * 5 * 4.186) + (416.641 * 846) + (29776.385 * 2260)

= 68278132.79 KJ/hr

Amount of steam required = Reboiler duty / Enthalpy of steam

= 68278132.79/2260

= 30211.5631 kg

Condenser duty calculation

Condenser duty = Reboiler duty – 7403700.205

= 68278132.79 – 7403700.205

= 60874432.59 kJ/hr

Mass of cooling water required = 60874432.59 / 4.186 * (343 - 298)

= 323164.158 kg

Input		Output	
Components	Energy(KJ/hr)	Component	Energy(KJ/hr)
C_2H_5OH	156907.067	Bottom	11983803.53
H_2O	10387004.36	Distillate	5963808.095
Reboiler duty	68278132.79		
Condenser duty	-60874432.59		
Total	17947611.62		17947611.62

Table 5.2 Energy balance over distillation column

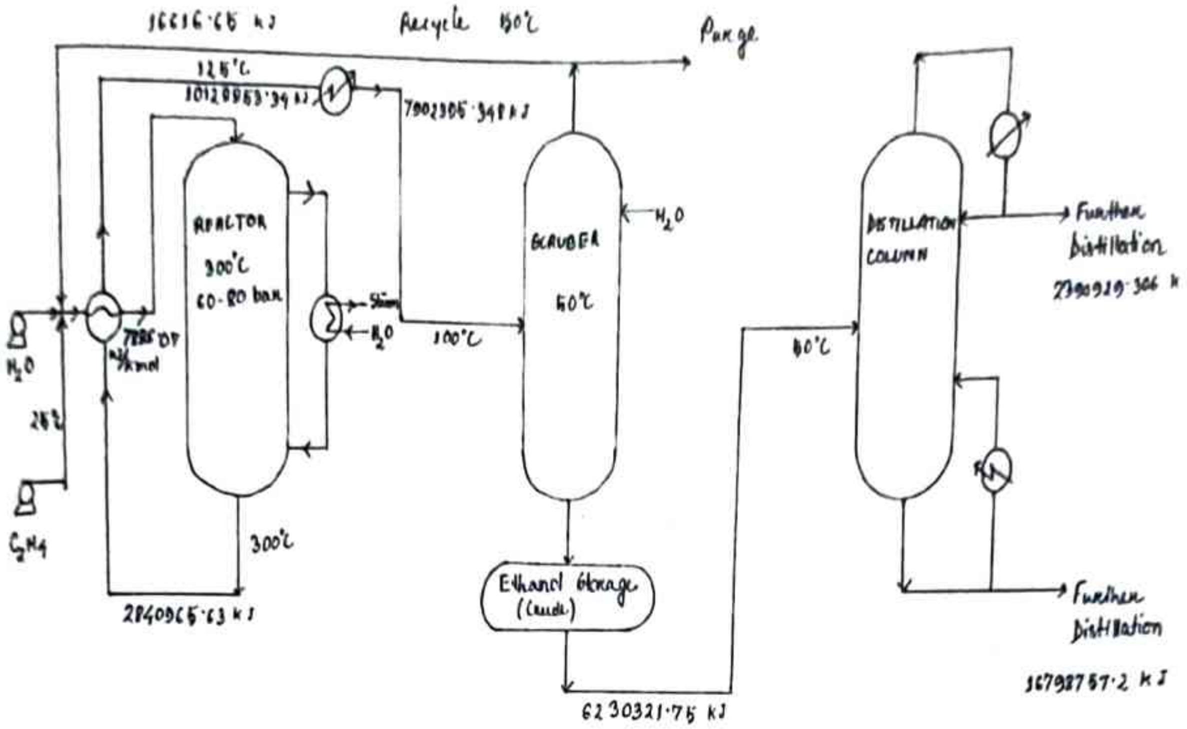

Fig. 5.1 Energy balance flow sheet

CHAPTER 6

EQUIPMENT DESIGN

6.1 HEAT EXCHANGER

Step 1: Heat Balance

Q_{hot} = 2110682.176 Btu/hr

Q_{cold} = 2110682.176 Btu/hr

Step 2: LMTD

	Hot Fluid	Cold Fluid	Difference
Higher Temperature	125	50	75
Lower Temperature	100	10	90
Differences	25	40	15

Table 6.1 LMTD calculation table

NOTE: All data's are taken from the book DQ KERN

$\Delta T1 = 100 - 10 = 90°F$ R = 0.625

$\Delta T2 = 125 - 50 = 75°F$ S= 0.347

LMTD = 180.35° F Ft =0.968

$\Delta t = 180.35*0.98 = 177.38°F$

U_D= 40 (Table 8)

$A = Q/(U_D \times LMTD) = 2110682.176/40*177.38$

A= 297.48 ft^2

Since 297.48 ft2 > 200 ft2

Therefore 1-2 Shell and Tube heat exchanger is used.

Step 3:

Assuming,

Shell Side	**Tube Side**
ID= 23 1/4	Number and length = 364, 8'0"
Baffle space = 12 in.	OD, BWG, pitch = ¾ in. , 16 BWG, 15/16 in. tri.
Passes = 1	Passes = 8

Table 6.2 Shell side & tube side data

Step 4: Temperature (tavg/tcal)

μ_{hot} = 0.009 Cp< 1 Cp

μ_{cold} = 0.01Cp < 1 Cp

∴ t_{avg} temperatures are used for each stream.

T_{avg}= 233.6 °F

t_{avg} = 86 °F

Step 5: Property Table

Property	**Hot Side**	**Cold Side**
C_p(Fig 2)	2.39	1.86
μ(Fig 15)	0.0242	0.022
K(Table 5)	0.0145	0.356
S(Table 6)	0.86	1
f	53.75	62.5

Table 6.3 Property table

Step 6: h_o and h_i calculation

Hot Fluid	**Cold Fluid**
$a_S = (ID \times c'B)/(144\ P_t) = 0.388\ ft^2$ $G_S = W/a_S = 8814.927$ $\mu = 2.42 \times 0.01 = 0.0242$ $De = 0.55/12 = 0.0458\ ft$ $Re_h = (De \times G_S)/\mu = 16682.79$ $jH = 200$ (fig 28) $h_o = jH(K/De)[(Cp \times \mu)/K]^{1/3}$ $= 37.05$ Btu/hr ft^2 °F	$a_t' = 0.302\ ft^2$ $a_t = (N_t \times a_t)/144\ n = 0.09547\ ft^2$ $G_t = W/\ a_t = 195323.29$ $V_t = G_t/(3600 \times f) = 0.868$ $\mu = 0.75 \times 2.42 = 1815$ $D = 0.62/12 = 0.0517$ $Re_c = (D \times G_t)/\mu = 463646.19$ $jH = 90$ $h_i = jH(K/D)[(Cp \times \mu)/K]^{1/3}$ $= 2668.72$ Btu/hr ft^2 °F $h_{io} = h_i \times (ID/OD)$ $= 82730.28$ Btu/hr ft^2 °F

Table 6.4 h_o and h_i

Step 7: U_c calculation

$U_C = (h_{io} \times h_o)/\ (h_{io} + h_o) = 42.51$ Btu/hr ft^2 °F

$U_C > U_D$

Step 8: Dirt factor calculation

$R_d = (1/U_D) - (1/U_C) = 0.00147$

Step 9: Pressure drop calculation

Shell Side (Hot)	Tube Side (Cold)
$f = 0.0019$ $N+1 = 8$ $Ds = 23.25/12 = 1.9375$ $\Delta P = (f \times G^2 \times Ds \times (N+1))/5.22 \times 10^{10} \times De \times s \times \Phi_s$ $= 0.098$ psi	$F = 0.00021$ $\Delta P = (f \times G^2 \times L \times n)/5.22 \times 10^{10} \times D \times s \times \Phi_s$ $= 4.47$ psi $\Delta P_T = 4nv^2/2gs = 3.52$ $\Delta P = 3.52 + 4.47 = 7.99$ psi

Table 6.5 Pressure drop calculation

Step 10: Summary

h_o	37.05 Btu/hr ft^2 °F
h_{io}	82730.28 Btu/ hr ft^2°F
U_C	42.51 Btu/hr ft^2 °F
U_D	40 Btu/hr ft^2°F
R_d	0.00147

Table 6.6 Summary table

6.2 Storage Tank

Basis : 1 Hr Operation.

We will design a storage tank for one month production capacity.

Assume 5% extra allowance in the volume of the tank.

Ethanol = 1041.533 kg/hr

= 1041.533 * 330 *24 kg/yr = 8248941. 36 kg/yr

Density of Ethanol = 789 kg/m^3

Tank volume=8248941.36 /789 m^3 + 5% excess volume

= (10454.93+ 522.74) m^3 = 10977.676 m^3

Assumptions

a. Annual cost of shell per unit area = C_1
b. Annual cost of bottom per unit area = C_2
c. Annual cost of roof per unit area = C_3
d. Annual cost of foundation per unit area = C_4

The following co-relations are taken as

a. $C_1 = 2C_2$
b. $C_3 = 1.8\ C_2$
c. $C_4 + C_5 = 0.4\ C_2$

Trial 1: Assuming it as a small tank

Optimum tank proportion = $D/H = 2C_1/(C_2 + C_3 + C_4 + C_5)$

- ⇨ $D/H = 4C_2/(C_2 + 1.8C_3 + 0.4C_2)$
- ⇨ $D/H = 1.25$
- ⇨ $D = 1.25\ H$
- ⇨ $V = \pi D^2H/4 = 3.14/4\ (1.25)^2H^3 = 1.22265\ H^3$
- ⇨ $10977.676\ m^3 = 1.22265\ H^3$
- ⇨ $H = (8978.5928)^{1/3}$

⇨ $H = 20.784\text{m} = 68.188\text{ft}$
⇨ $D = 25.9804\text{m} = 85.237 \text{ ft}$

Assuming double butt joint, condition: $D(H-1) \geq 1720$

$D(H-1) = 85.237(68.188-1) = 5726.986 > 1720 \text{ ft}^2$

So, our assumption of small tank is not correct.

Trial 2: Assuming it as a large tank.

Optimum tank proportion = $D/H = 4C_1/(C_2+C_3+C_4+C_5)$

⇨ $D/H = 8C_2/(C_2+1.8C_3+0.4C_2)$
⇨ $D/H = 2.5$
⇨ $D = 2.5 H$
⇨ $V = \pi D^2H/4 = 3.14/4\ (2.5)^2H^3 = 4.90625\ H^3$
⇨ $10977.676\text{m}^3 = 4.90625\ H^3$
⇨ $H = (2237.486)^{1/3}$
⇨ $H = 13.079\text{m} = 42.910 \text{ ft}$
⇨ $D = 32.694\text{m} = 107.278 \text{ ft}$

Assuming butt joint, condition: $D(H-1) \geq 1720 \text{ ft}^2$

$D(H-1) = 107.278(42.910-1) = 4496.020 > 1720 \text{ ft}^2$

The condition is satisfied. Hence, it is a large tank.

Design Data

$D = 32.694\text{m}$

$H = 13.079 \text{ m}$

MOC - 20 Mo 55 (Appendix A Table A-1 of B.C Bhattacharya).

$S = 1.40 * 10^8 \text{ N/m}^2 = 1.427 * 10^3 \text{ Kgf/cm}^2$

$J = 0.85$

Sp gr=1

Corrosion allowance = 0.3mm

Tank circumference = $\pi D = 3.14 * 32.694 = 102.659\text{m}$

Effective circumference = $\pi D - (2n * 10^{-3}) = 102.659 - (2n * 10^{-3})$

$L = [102.659 - (2n * 10^{-3})]/n$

Now, let us assume n= 9 (Trial 1)

$L = [102.659-(2*9*10^{-3})]/9 = 11.404$ m (not in the 6-10m range)

Let = 12 (Trial 2)

$L = [102.659-(2*12*10^{-3})]/12 = 8.55$ m (in the 6-10m range)

Now, standard width

$H/n = 13.079/12 = 1.0899$m

= 1089mm = 1100 mm (Approx) = 1.1 m (Appendix B, B.C Bhattacharya)

Calculation of thickness sections

$t_i = [50(H-0.3)D*Sp\ Gr.]/(S*J)$

$t_1 = [50(13.079-0.3)32.694*1]/(0.85*1.427*10^3\ Kgf/cm^2) = 17.22$ mm

$t_1 + t_c = 17.22 + 0.3 = 17.52$ mm $t_1' = 18$ mm

$t_2 = [50(11.979-0.3)32.694*1]/(0.85*1.427*10^3\ Kgf/cm^2) = 15.73$ mm

$t_2 + t_c = 16$ mm $t_2' = 16$ mm

$t_3 = [50(10.879-0.3)32.694*1]/(0.85*1.427*10^3\ Kgf/cm^2) = 14.25$ mm

$t_3 + t_c = 14.55$ mm $t_3' = 16$ mm

$t_4 = [50(9.779-0.3)32.694*1]/(0.85*1.427*10^3\ Kgf/cm^2) = 12.77$ mm

$t_4 + t_c = 13.07$ mm $t_4' = 14$ mm

$t_5 = [50(9.479-0.3)32.694*1]/(0.85*1.427*10^3\ Kgf/cm^2) = 12.37$ mm

$t_5 + t_c = 12.67$ mm $t_5' = 14$ mm

$t_6 = [50(9.179-0.3)32.694*1]/(0.85*1.427*10^3\ Kgf/cm^2) = 11.96$ mm

$t_6 + t_c = 12.26$ mm $t_6' = 14$ mm

$t_7 = [50(8.879-0.3)32.694*1]/(0.85*1.427*10^3\ Kgf/cm^2) = 11.56$ mm

$t_7 + t_c = 11.86$ mm $t_7' = 12$ mm

$t_8 = [50(7.779-0.3)32.694*1]/(0.85*1.427*10^3\ Kgf/cm^2) = 10.07$ mm

$t_8 + t_c = 10.37$ mm $t_8' = 11$ mm

$t_9 = [50(6.679-0.3)32.694*1]/(0.85*1.427*10^3\ Kgf/cm^2) = 8.579$ mm

$t_9 + t_c = 8.897$ mm $t_9' = 9$ mm

$t_{10} = [50(5.579-0.3)32.694*1]/(0.85*1.427*10^3\ Kgf/cm^2) = 7.11$ mm

$t_{10} + t_c = 7.41$ mm $t_{10}' = 8$ mm

$t_{11} + t_c = 5.93$ mm $t_{11}' = 6$ mm

$t_{12} = [50(3.379-0.3)32.694*1]/(0.85*1.427*10^3\ Kgf/cm^2) = 4.14$ mm

$t_{12}+t_c = 4.44$ mm $t_{12}' = 6$ mm

According to clause 6.3.3.2 of B.C Bhattacharya if diameter is in between (15-36)m then the minimum thickness of the section should be 6mm . Hence thickness of the section 12 is 6mm.

Thickness sections	t_{cal} mm	H , m	t', mm	t_{std} mm
1	17.22	15.479	17.52	18
2	15.73	14.379	16	16
3	14.25	13.279	14.55	16
4	12.77	12.179	13.07	14
5	12.37	11.079	12.67	14
6	11.96	9.979	12.26	14
7	11.56	8.879	11.86	12
8	10.07	7.779	10.37	11
9	8.579	6.679	8.897	9
10	7.11	5.579	7.41	8
11	5.93	4.479	5.93	6
12	4.14	3.379	4.44	6

Table 6.6 Thickness of Section

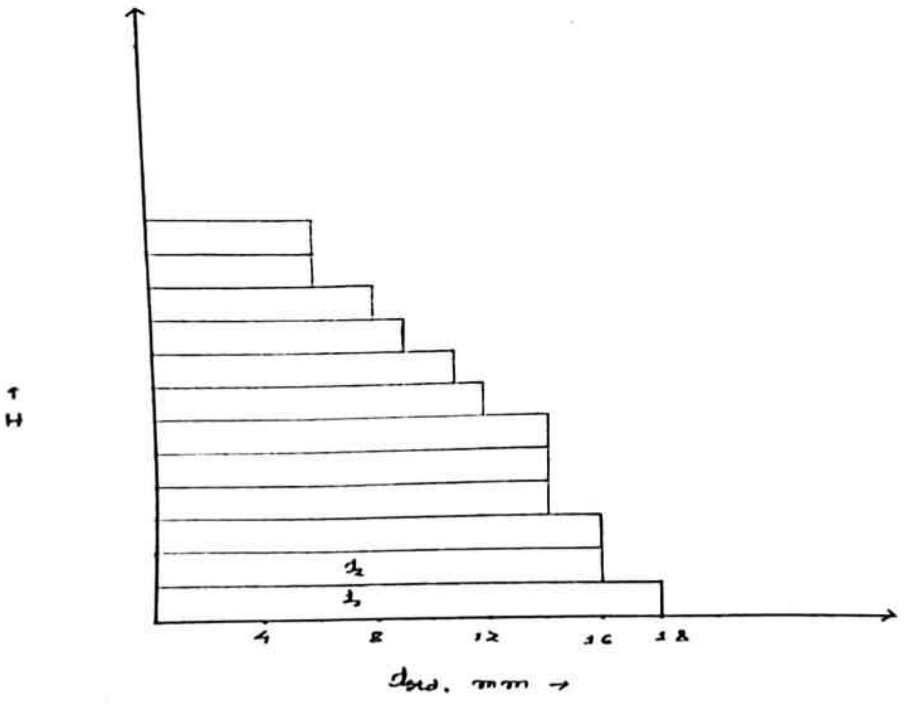

Fig. 6.1Thickness of section

CHAPTER 7

CONCLUSION

Our Chemical Engineering project design was aimed to bring forth an integrated detailed design for the 'Production of Ethanol from ethylene'. This project covered several aspects of the plant's design including firstly a literature background on the production of ethanol through different routes. Rigorous comprehensive mass and energy balances were done throughout the plant. The next task was the detailed design of two of the plant's equipment including the heat exchanger and storage tank. The guidance and support from our guide Dr. Tapan Jyoti Sarma is much appreciated and the knowledge they passed on to us is something to be cherished and for that we express our deep gratitude.

CHAPTER 8

REFERENCE

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CHAPTER 9

APPENDIX

9.1 MATERIAL SAFETY DATA SHEET ETHANOL

a) HAZARDS IDENTIFICATION SUMMARY

KEEP OUT OF REACH OF CHILDREN – WARNING - POISON – Always

Keep containers tightly closed to prevent escape of the ethanol and loss of strength. Causes irritation of the skin, eyes, nose, and throat. Avoid exposureto fumes and contact with skin, eyes and clothing. Avoid prolonged orrepeated contact and breathing of vapour. This product is clear, colourless liquid with pungent odour.

b) FIRST AID MEASURES

If in eyes: If splashed in eyes, wash freely with water for 15 minutes. Seekmedical attention.

If on skin: Wash thoroughly with soap and water.

If swallowed: Give a weak solution of ammonia, then egg white or milk.Induce vomiting by inserting finger down the throat; repeat 3 times.

Give stimulants and demulcents such as gruel or flour and water. Call apoison control centre or doctor immediately for treatment advice.

If inhaled: Remove person to fresh air. Have person lie down and keepquiet and warm. Give egg white or milk. Call a poison control centre ordoctor for further treatment advice.

c) FIRE FIGHTING MEASURES

FLASH POINT (°C/Test Method): 55°F

FLAMMABLE LIMITS (LFL & UFL): LFL: 3.3% - UFL: 19%.

HAZARDOUS COMBUSTION PRODUCTS: Moderate fire and explosion hazard when exposed to heat or flame.

EXTINGUISHING MEDIA: Use medium appropriate to surrounding fire. Use dry chemical, "alcohol foam", carbon dioxide, or water in flooding amounts as fog. Solid streams may not be effective.

SPECIAL FIRE FIGHTING PROCEDURES: Wear self-contained breathing apparatus with full protective clothing. Fight fire from upwind and keep all non-essential personnel out of area of intense smoke.

UNUSUAL FIRE AND EXPLOSION HAZARDS: Empty containers may contain explosive vapours. If water is used to fight fire and/or cool containers, contain runoff, using dikes to prevent contamination of water supplies.

d) HANDLING AND STORAGE

HANDLING: Wash hands before eating, drinking, chewing gum, using tobacco or using the toilet. Remove clothing immediately if pesticide gets inside. Then wash thoroughly and put on clean clothing. Remove PPE immediately after handling this product. Wash the outside of gloves before removing. As soon as possible, wash thoroughly and change into clean clothing.

STORAGE: Store in original container only. Do not store below 15OC as precipitation may occur. Keep container tightly closed when not in use. Store away from seeds, fertilizer, plants, and foodstuffs. Do not contaminate water, food or feed by storage or disposal.

Personal Protective Equipment: Applicators and other handlers must wear: long sleeved shirt and long pants, wear a suitable NIOSH/MSHA approved respirator with organic vapour cartridges or wear self-contained breathing apparatus to prevent inhalation of gas fumes, rubber or chemicalresistant gloves, rubber boots plus socks, and protective eyewear. Follow manufacturer's instructions for cleaning and maintaining PPE. If no such instructions for washables, use detergent and hot water. Keep and wash PPE separately from other laundry. After each day of use, clothing or PPE must no be reused until it has been cleaned.

e) Hess Law : Hess law can be used to determine the overall energy required for a chemical reaction that can be divided into synthetic steps that are individually easier to characterize. This affords the compillation of standard enthalpies of formation , which may be used to predict the enthalpy change in complex systhesis .

f) Boiling Points:

COMPONENTS	BOILING POINTS(°C)
C_2H_5OH	78.37
C_2H_4	103.7
CH_3CHO	20.2
$(C_2H_5)_2O$	34.6
C_2H_2	-84
H_2O	100

Table 9.1 Boiling Points of Compounds Used