PART- I

PART - I

REMOVAL, RECOVERY AND UTILIZATION OF WASTE MATERIALS (ORGANICS AND INORGANICS) FROM CAPROLACTAM EFFLUENT

General

Caprolactam is one of the Petrochemical products, largely used as raw material for nylon-6, the Polyamide fibres for clothing. Caprolactam is also used for the manufacturing of lysine, a nutrient-building block for protein synthesis. Thus it is more popular because of low cost and many industrial applications. Its process is closely integrated with fertilizer production and hence is more economically suited for fertilizer complexes.

Production of caprolactam by EMS industries Ltd., Switzerland; started in 1951 with 600 T/A plant using phenol as raw material and by early sixities put up another plant of 100,000 T/A capacity using Benzene or cyclohexane as raw material [50]. Annual world production during 1986 was about 27,88,000 tons. The major producers of caprolactam are USA, W.Germany, Japan, Belgium, Netherland and Italy as stated in Table-6 [51].

In 1963 India started the production of Nylon-6 for industrial uses from imported caprolactam. Gujarat State Fertilizers Company Limited (G.S.F.C.), Baroda, started caprolactam plant of 20,500 tons/annum capacity, production based on Inventa process-selecting benzene as raw material, in 1974. As per the latest report, GSFC has planned to increase this production to 50,000 MT per annum to accelerate availability of indegeneous raw material for Nylon industry and help in saving substantial and valuable Foreign Exchange.

In addition to this rupees 148 crores worth caprolactam project of public sector, Fertilizer and Chemicals, Travencore Ltd., is to be commissioned in April 1989. The project envisages production of 50,000 Tons of caprolactam and 225,000 tons of Ammonium sulfate per annum.

Chemistry involved in the production of caprolactam by GSFC is schematically represented in Fig.7.

TABLE - 6

WORLD PRODUCTION CAPACITY (COUNTRY-WISE) OF MAN-MADE FIBRE RAW MATERIALS.

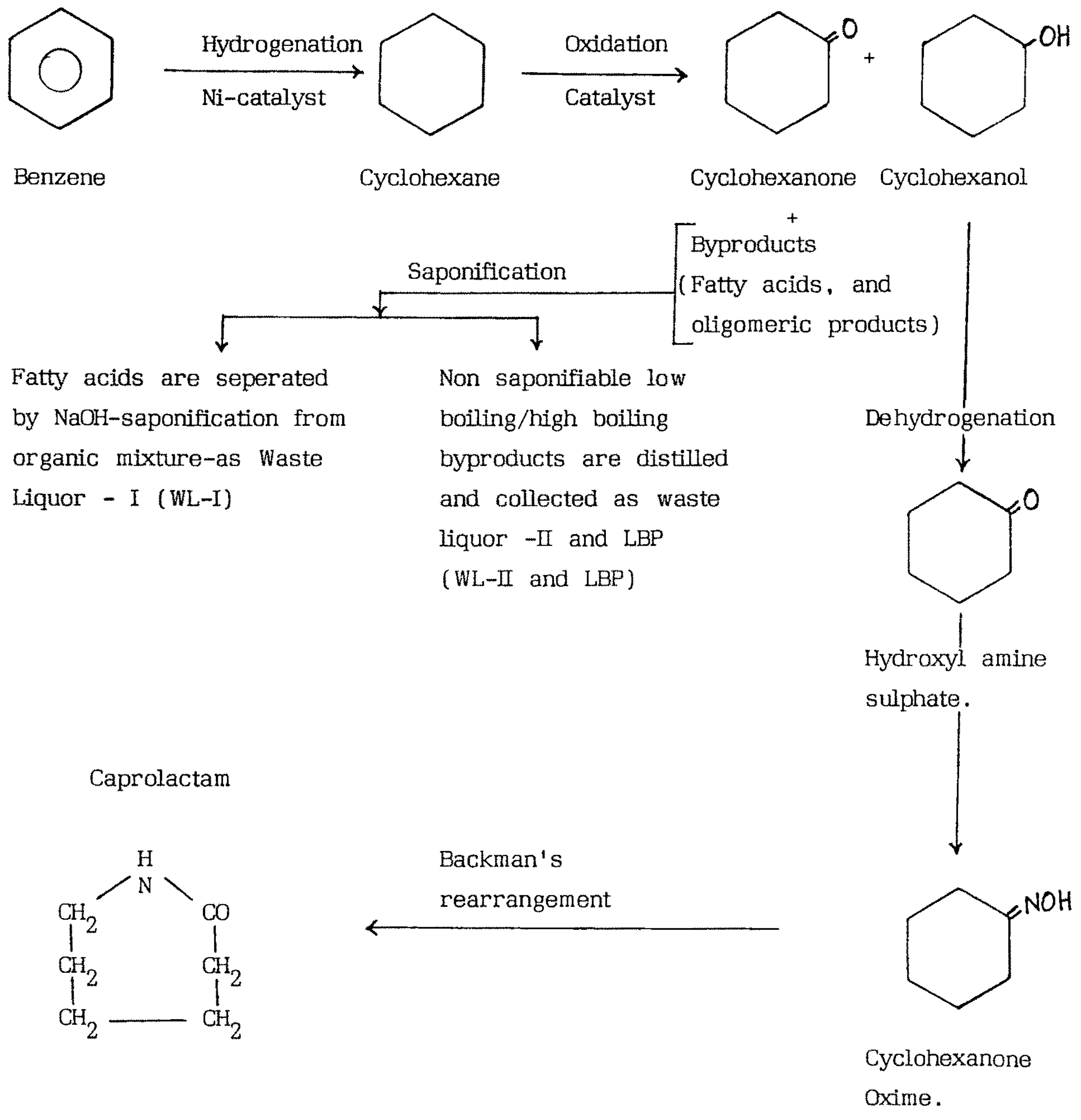
(Unit : 1000 Tonnes/Annum)

CAPROLACTAM

Country	End of 1984	End of 1985	End of 1986
Belgium	240	240	240
Brazil	35	70	70
Bulgaria	30	30	30
China	10	10	10
Colombia	17	60	60
Czechoslovakia	70	70	70
G.D.R.	60	60	60
Hungary	20	20	20
India	20	20	20
Italy	198	198	198
Maxico	45	145	145
Netherlands	220	220	220
Poland	100	100	100
Romania	40	40	40
South Korea	40	40	40
Spain	30	30	30
Switzerland	16	16	16
Taiwan	100	100	100
Turkey	25	25	25
U.S.A.	549	549	549
U.S.S.R.	380	540	540
West Germany	200	200	200
Yugoslavia	5	5	5
World Total (excluding Japan)	2,450	2,788	2,788

Source : Survey by Japan Chemical Fibres Association.

REACTIONS



Fatty acids are seperated by NaOH-saponification from organic mixture-as Waste Liquor - I (WL-I)

Non saponifiable low boiling/high boiling byproducts are distilled and collected as waste liquor -II and LBP (WL-II and LBP)

Figure - 7

Reference to Fig.7 shows that over and above the main intermediates like cyclohexane and cyclohexanone, there are number of by-products which are formed during oxidation process.

Some of the by-products, acidic in nature are removed by saponification process with sodium hydroxide. Mixture of cyclohexanone and cyclohexanol is fractionally distilled and by-product labelled as LBP (Low boiling product) and HBP/HOP (High Boiling Product/High Oxidation Product) are obtained. Solution of sodium salt of mix fatty acids is labelled as WL-I. The residue left after the saponification and fractional distillation is labelled as WL-II.

The analytical data of WL-I and WL-II is given in Table-7 and Table-8 respectively [52].

TABLE - 7

Physical and Chemical properties of WL-I [52].

(1)	Colour	:	Reddish brown coloured liquid.
(2)	Odour	:	Free ammonia and organic.
(3)	Density Kg/m^3, 15°C	:	1.02
(4)	Nature	:	Toxic and corrosive.
(5)	Calorific value	:	1100 K.Cal/Kg.
(6)	Quantity generated	:	2250 Kg/hr (54 T/day)
(7)	pH	:	Highly alkaline ranges from 11.0 to 11.3

Approx. constituents of WL-I are Na-salts of organic acids, sodium carbonate, free caustic soda (approx. 25% to 30% by weight) and balance water.

Na-Salt	**Weight %**
Na-Butyrate	4 %
Na-Valerate	19 %
Na-Caproate	6 %
Na-Succinate	5 %
Na-Glutarate	8 %
Na-Adipate	17 %
Na-Oxycaproate	26 %
Na-Slats from polymer oxycaproic and oxo acids.	15 %

In addition to all above, sodium salts of few more following mono-carboxylic acids are present in small quantities [53].

Acetic acid
Propionic acid
Iso-butyric acid
E-caprolactone
3-Oxo butanoic acid
4-Oxo pentanoic acid
5-Hydorxy valeric acid
4-Hydroxy butanoic acid
3-Oxo pentanoic acid
4-Hydroxy valeric acid

Moreover, sodium salt of few more dicarboxylic acids like oxalic acid, malonic acid are present in small quantities.

To understand the load of the effluent, total residue was determined as per standard methods [13]. Results are summarised as under:

Total residue (Total solids) of WL-I ranges from 346 gm to 363.2 gm per litre. Total volatile solids ranges from 220.0 gm to 221.4 gm per litre of WL-I.

TABLE - 8

Waste Liquor - II (WL-II) : Physical and Chemical properties [52].

(1)	Density Kg/m^3 at 15°C	0.9843
(2)	Calorific value	9660 K.Cal/Kg.
(3)	Nature	Corrosive and Toxic
(4)	Water and sediments	0.03 %
(5)	Quantity generated	400 Kg/hr (9.6 T/day)

It is a grease like reddish brown semisolid material which contains mainly LBP. HBP/HOP. Thus it contains

low boiling point product	15 %
Cyclohexanone	10 - 15 %
Cyclohexanol	15 - 20 %
High oxides products	60 - 70 %

LBP mainly consists of pentanols (50%), caproic aldehyde (30%) and the rest are butanol, cyclopentanone, cyclopentanol etc..

Low boiling fraction of LBP is labelled as LBP-T_1 (collected from caprolactam plant in GSFC).

At present GSFC uses its incineration plant to dispose off WL-I and WL-II. WL-II has high calorific value, hence WL-II, WL-I and fuel oil in respective proportions are used for effective burning. The waste liquor incinerator was installed at the cost of Rs.260 lakhs and is lined with chromium [52].

Prior to incineration WL-I is concentrated from 25% solid to 45% solid with the help of steam generated in boilers at 15 Kg pressure. Incinerator is designed to burn 400 Kg/hr WL-II and 2250 Kg/hr WL-I.

The flue gas after combustion in the furnace is scrubbed in soda solution to decrease the temperature of the gas from 700-800°C to 70-80°C and to remove particulate matters. Thus clean flue gas is discharged to the atmosphere from a chimney with the help of induced draft blower. During this process small amount of soda ash is recovered as by-product.

35000 NM^3/hr is the rate of gase which is discharged to atmosphere. This gas mainly contains Nitrogen, carbon dioxide, moisture and some volatile organics.

A definite recurring amount is being spent to run the incinerator.

The incineration solves some of the problems of water pollution by burning large quantities of organics. However, it creates more problems in air pollution and thermal pollution. Moreover, a positive approach of solving the disposal of WL-I can help to save WL-II, having great potential for utility, and saving of extra fuel which is being used to burn WL-I and WL-II. The incineration unit continuously faces problem of corrosion as the by-products are acidic. The high quantity of inorganics in the effluent creates many operational problems due to chocking of pipelines and valves, nozzles etc. We are already polluting air by number of ways, hence addition of such a huge quantity of CO_2 will definitely disturb the ecosystem. One of the major objections of CO_2 is increase in the atmosphere temperature by absorbing IR radiation. All the countries of the world are becoming cautious to protect ozone layer.

In the present study main emphasis will be on the treatment of WL-I. The separation and utilization of organics from the WL-I would prove to be more fruitful compared to incineration.

Inhouse R & D department has tried some aspects of utilization of couple of constituents of WL-II and WL-I. However, the efforts to recover all the organics of WL-I are yet lacking.

The terms used in the analytical section

(1) BOD : Biochemical Oxygen Demand is the amount of dissolved oxygen, consumed in 5 days by biological processes breaking down organic matter in effluent at 20°C.

(2) COD : Chemical Oxygen Demand is a measure of the oxygen required to oxidize all compounds in water, organic and inorganic, with the help of strong chemical oxident.

(3) TOC : Total Organic Carbon is quantitative measurement of carbon element present only due to organic matters present in waste water. This is done by burning sample and estimating CO_2.

(4) TS : Total Solids (Total Residue) is defined as the sum of the homogeneous suspended and dissolved material in a waste water sample.

(5) Total volatile solids (TVS) : Total volatile residue (Total Volatile Solids) is the residue obtained from the determination of total residue after it is ignited at 550°C in muffle furnace. The loss of weight on ignition is reported as mg/l total volatile residue.

(6) Total Carbon (TC) : Quantitative measurement of carbon element present due to organic or inorganic matters in waste water.

TC - TOC = Inorganic Carbon.

WL-I contains mainly salts of organic acids (Table-7). The removal and recovery of organics has to be monitored to assess the working of a procedure. This involves the COD analysis of large number of samples. The recovered oil is also to be tested for its constituents, if possible. In the present study following methods were used for the analysis of different products at different stages.

1. GENERAL EXPERIMENTAL ASPECTS

In all analytical work Corning, Borosil glassware were used. Certified micropipettes were also used. Standard Analytical Grade Chemicals and reagents of well reputed companies were used. In case of samples having high concentration of organics and inorganics, samples were accurately diluted to bring it in the range of analysis. Repeated analysis could produce reliable and consistent results.

1.1 TOC analysis

Certain samples for TOC and TC were analysed by Dohrmann Carbon Analyser Horiba PIR-2000 Japan Pat. 873118, U.S. Pat. 3729264 and few more samples were analysed for TOC by Beckman TOC Analyser, U.S.A. model - 915 - B.

For TOC sample is filtered, acidified with 1:1 HNO_3 and then purged with N_2 gas and analysed. For TC sample is filtered and analysed (Table 38 and 39).

Instrument was standardized with 2000 ppm potassium phthalate solution. Analysis was carried out by Standard procedure given in the booklet of this instrument.

1.2 Gas Liquid Chromatography

Hewlett Packard 5793 A series Gas Chromatograph equipped with 3390-A integrator, Carbowax 20 M on chromosorb - W Coloumn-10%, column length - 6', dia - 1/8" OD stainless steel tube was used to take GLC of certain important samples to know the constituent removed of volatile organics in each treatment stage (Fig. 11 to 16).

1.3 Biochemical Oxygen Demand (BOD) [13].

The sample of waste or an appropriate dilution is incubated for 5 days at 20°C in the dark. The reduction in dissolved oxygen concentration during the incubation period yields a measure of the BOD. Measurement of oxygen carried out by titration method using standard sodium thiosulfate solution. Procedure to be used is found in standard methods for the examination of water and waste water in 14th edition. This is time consuming test and depends on the acclimatized seed, nutrients and nature of the organics present in the test solutions. Very few samples were analysed for BOD.

1.4 Total solid and total volatile solids are analysed as per the standard methods [13].

1.5 Chemical Oxygen Demand (COD) [13].

In COD, organics are oxidized up to 95 to 100 % of theoretical value. COD determination has an advantage over BOD determination in that the result can be obtained in about 5 hours as compared to 5 days required for BOD test. Further the test is relatively easy, gives reproducible results and is not affected by minor impurities as the BOD test. Hence more weightage has been given in this work on COD test.

The organic matter gets oxidized completely by Potassium dichromate in the presence of H_2SO_4 to produce CO_2 + H_2O. The excess of $K_2Cr_2O_7$ remaining after the reaction is titrated with standard ferrous ammonium sulfate solution. $Fe(NH_4)_2(SO_4)_2.6H_2O$. using Phenanthroline ferrous sulfate (ferroin) indicator solution. The dichromate consumed gives the oxygen required for the oxidation of organic matters.

Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion flask prior to addition of other reagents to complex the chlorides, thereby effectively eliminating the interference. Thus Cl ions ties up as a soluble mercuric chloride complex and greatly reduces its ability to react further.

Addition of Ag_2SO_4(silver sulfate) to conc. H_2SO_4 as a catalyst stimulates the oxidation of straight chain aliphatic and aromatic compounds. About 0.4 gm of $HgSO_4$ is adequate to complex 40 mg Cl ions in the form of poorly ionized $HgCl_2$.

Placed several boiling stones in reflux flask followed by 50.0 ml of sample or an aliquot diluted to 50 ml and added 1 gm of $HgSO_4$. 5 ml conc. H_2SO_4 was added and until the $HgSO_4$ got dissolved. The reflux flask was placed in an ice bath to prevent loss of volatile materials due to generated heat. Then added $K_2Cr_2O_7$ standard solution and 70-80 ml of of sulfuric acid - silver sulfate solution. Heat was applied to the flask and refluxed for 2 hours. Allowed the flask to cool, washed down condeser with distilled water and cooled the solution to about room temperature. 8 to 10 drops of ferroin indicator were added to the solution and titrated the excess dichromate with 0.25 N ferrous ammonium sulfate solution to the end point.

The colour change was sharp, changing from a blue-green to a reddish hue. Simultaneously ran a blank determination following same procedure.

CALCULATION :

$$\text{COD mg/litre} = \frac{(A-B)N \times 8000}{S}$$

A = ml of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the blank.

B = ml of F.A.Sulfate solution required for titration of the sample.

N = Normality of F.A. sulfate solution.

S = ml of sample used for the test.

1.6 **Analysis of free mineral acid, sodium sulfate and Ammonium sulfate** [54,13].

Per cent Na_2SO_4 was analysed by standard gravimetric method for sulfate analysis. Free sulfuric acid was calculated by simple acid base titration using an indicator.

Percentage of ammonium sulfate was analysed by analysing ammonical nitrogen content by distillation and absorbing free amonia in boric acid [13]. Digital flame photometer was used to estimate sodium ion concentration in Na_2SO_4 salt and in final effluent.

2. SEPERATION OF ORGANIC MATERIALS FROM WASTE LIQUOR - I (WL-I)

Waste liquor-I contains sodium salt of acids. Acidification of WL-I will generate free-fatty acids. Some of the fatty acids are soluble in water, hence it would be difficult to obtain ideal separation condition. However, looking to the huge amount of aqueous phase, it would be necessary to keep COD value of aqueous phase as low as possible.

Preliminary work :

For the separation of fatty acids number of common approaches were tried.

2.1 WL-I was acidified to different pH by conc. HCl or conc. H_2SO_4 to generate free acids. After that different inorganic flocculating agents were tried.

The experiments suggested that due to high concentration of fatty acids, it would be difficult to separate and isolate them as salts (or flocks) of calcium or other anions.

2.2 Generally oxidizing agents are tried to decompose organic matters of effluent [55-60]. Most of the organics of WL-I are fatty acids. However, it was proposed to try oxidizing agents like H_2O_2, HNO_3, chlorine etc. to see its effect in reducing the COD value. The experiments suggest that these oxidizing agents do not play effective role in the reduction of COD value as these organics are quite stable against small quantities of oxidizing agents.

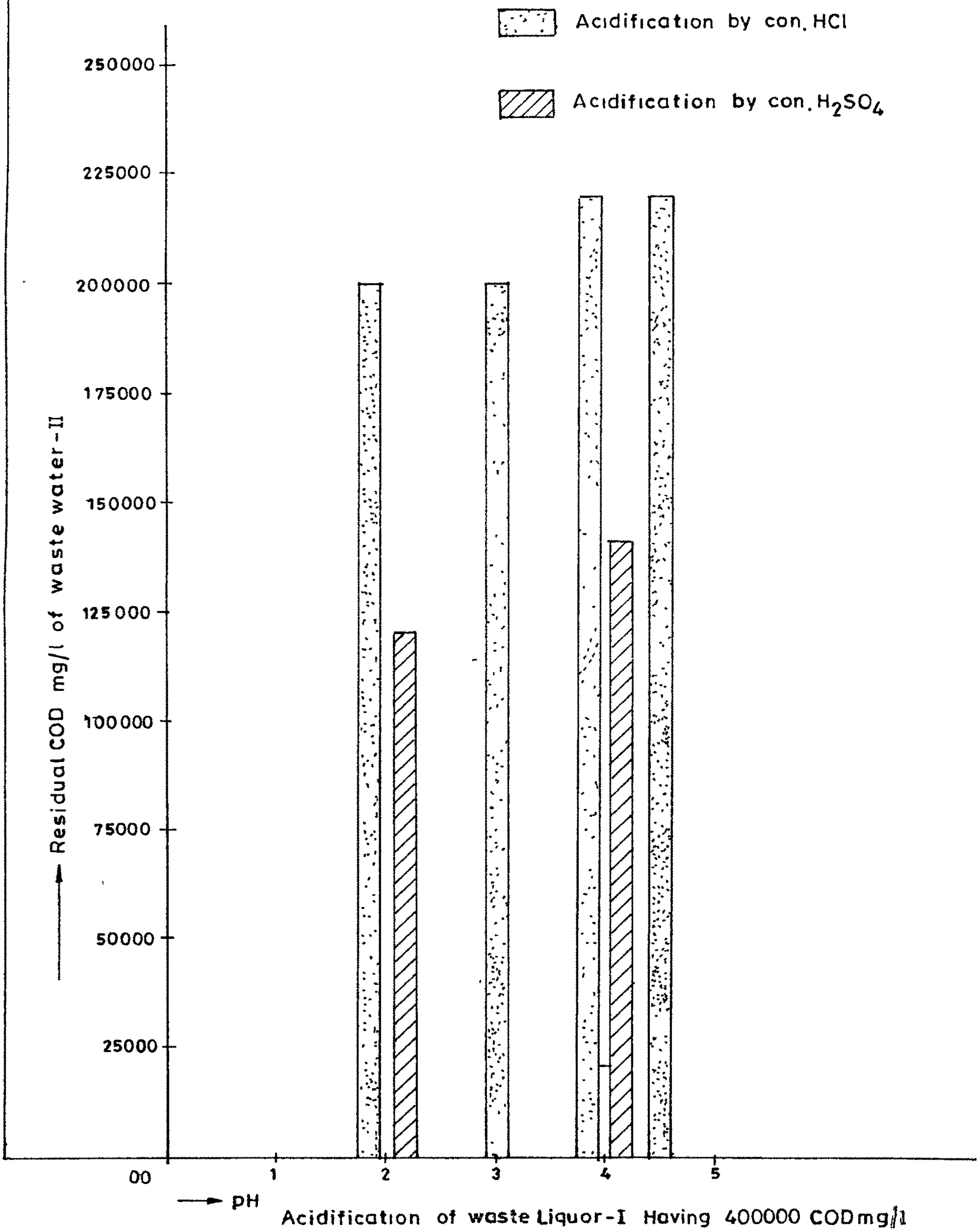
2.3 Separation of fatty acids by acidification.

WL-I was acidified at different pH and the effect of pH was studied on the effective separation of fatty acids from the aqueous phase. The effective separation was monitored by estimating COD value of effluent (W.W.-II) obtained after the removal of organic layer. Higher the COD value, the separation is less effective at the respective pH.

For the acidification, conc. HCl as well as conc. H_2SO_4 were tried to see the effectivity of these acids in the separation of fatty acids (organic oil).

The data obtained at different pH are graphically recorded in Fig. 8 for HCl and H_2SO_4.

Figure : 8



Acidification of waste Liquor-I Having 400000 COD mg/l

The reference to Fig.8 indicates that fatty acids starts separating from pH 4 onwards. At pH 3, removal of organics is intermediate. Most effective separation is achieved at pH 2, where conc.H_2SO_4 is used as a acidifying agent. The efficiency of removal of organics is much higher in the process where conc. H_2SO_4 is used compared to conc. HCl.

This can be understood as nutralization with HCl will generate NaCl, whereas with conc. H_2SO_4, Na_2SO_4 will be produced in the solution. The salting out effect of Na_2SO_4 is much more compared to NaCl due to solubility differences of these two salts. Moreover, the amount of conc. H_2SO_4 required to raise the pH upto 2 is much less compared to conc. HCl. Due to this reason dilution of WL-I during neutralization is much less in the case of conc. H_2SO_4.

Based on these results in the other experiments conc. H_2SO_4 was used to raise pH of WL-I from alkaline to acidic.

These experiments suggested that conc. H_2SO_4 and pH 2 are most effective for the separation of organic acids (Orgnic oil) from WL-I.

The experiments involved the analysis of each sample, after separation of organics, in terms of COD value of WW-II. The original COD value of WL-I is in the range of 390000 mg/l to 420000 mg/l due to variation in samples collected from WL-I storage tank in GSFC.

The COD value of WW-II after removal of fatty acids by acidification with conc. H_2SO_4 ranges from 1,10,000 to 1,25,000 mg/l.

These COD values of WW-II are much higher for the disposal as effluent. Moreover, the bio-oxidation processes can not be used to destroy organics from the WW-II due to very high COD value. Even, dilution would be quite uneconomical to reduce COD values for the biodegradation.

WW-II contains good amount of Na_2SO_4 and the recovery of Na_2SO_4 can make the effluent treatment more feasible.

Due to all these reasons efforts were concentrated in further removal of organics from WW-II so as to make the whole system viable for operation.

3. OPTIMIZATION OF SEPARATION OF ORGANIC OIL FROM WL-I

It has been described how better separation of organic oil takes place at pH 2 from the WL-I. However, high COD values of WW-II indicates that separation is not complete. Due to this reason number of variations were tried to optimise the recovery of organic oil (fatty acids) from the WL-I.

In all these attmpts pH 2 of WL-I was maintained.

3.(a) Effect of time after acidification to pH 2 on the separation of organic oil.

It was decided to study whether more amount of organic oil separates on standing from WW-II. For this purpose WL-I was acidified to pH 2 by using conc. H_2SO_4 . The organic layer was separated. The aqueous layer, (WW-II) was allowed to stand. It was observed that on standing more oil separates and the aqueous phase obtained after removal of oil has lower COD values. To study the effective separation of residual organic liquid on standing the samples of WW-II were allowed to stand for 9,20, and 24 hours. The results indicated that 20-24 hours period was best to separate residual oil from WW-II. These observations were achieved by measuring COD value of WW-II at different interval of time.

From these preliminary observations, a large scale experiment was kept to verify the preliminary observation. 1 litre of WW-II were allowed to stand fro 24 hours; which gave best results. However, for other working, 6 to 9 hours standing time gave quite reasonable separation of residual oil.

3.(b) **Effect of added salt on the separation of organic oil** (salting out effect)

It was thought to study the effect of added salt in WW-II on the separation of organic oil. Most of the residual oil seems to be dissolved in aqueous phase. Addition of the salt being more soluble pushes organic oil out of the solution. Sodium sulphate was added to WW-II. It was found that due to salting out effect more amount of organic liquid separated. The data is given in Table-9.

TABLE-9

Effect of salt on the separation of organic oil.

WW-II	**Separation of oil from WW-II**
(A) 1 litre of WW-II allowed to stand for 24 hours.	16 to 18 ml oil.
(B) 1 litre WW-II + 110 g Na_2SO_4* and allowed to stand for 24 hours.	36 ml of oil.

*stirred the solution till Na_2SO_4 is dissolved.

3.(c) Effect of de-emulsifying agent on the seperation of organic oil.

Number of de-emulsifying agents were used for the recovery of oil from aqueous/oil mixture. They are also used in the removal of traces of oil from water which is obtained from oil wells. It was proposed to use different de-emulsifying agents commercially available to optimize the separation of oil when WL-I is acidified. Following de-emulsifying agents were tried.

HDL - 5700
HDL - 6800
JM - 5555
HDL - 8204
JM - 444
SWANIC - ES - 9
Nopco DMF - 300
HDL - 8203
Di-trolite DE - 205 - 15

HDL is Trade name of M/s. Hico Products Ltd., Bombay.
JM is Trade name of M/s. Jirad Chemicals, Bhavanagar.
Di-trolite is trade name of M/s. Daichi Carkari Ltd., Bombay.

These de-emulsifying agents were collected from ONGC, Baroda to evaluate the effect of these de-emulsifying agents on the separation of organic oil.

In each experiment 1 litre of WL-I was taken in a beaker, it was acidified up to pH 2 and then de-emulsifying agent was added. The amount of de-emulsifying agent was varied from 0.03% to 0.1%.

After that, the organic oil was separated and WW-II (aqueous phase) was collected. The COD value of WW-II was determined in each experiment. One blank experiment was also carried out. The results indicated in Table-10 reveal that the addition of de-emulsifying agent does not reduce effectively the COD value of WW-II.

It was also observed that separation time of organic oil from WL-I could not be decreased.

TABLE - 10

COD value of WW-II obtained after the addition of de-emulsifying agent to WL-I during acidification.

	De-emulsifying agent	**COD value in mg/l**
01.	Blank (without De-emulsifying agent)	110,400
02.	HDL - 5700	106,900
03.	HDL - 6800	104,240
04.	JM - 5555	110,000
05.	HDL - 8204	109,500
06.	JM - 444	107,460
07.	SWANIC - ES - 9	103,780
08.	NOPCO - DMF - 300	105,100
09.	HDL - 8203	106,220
10.	Di-trolite DE - 205 - 15	103,900

3.(d) Use of liquid ion-exchanger as flocculant

LIE was added to WW-II, stirred for few minutes and allowed to stand for few hours to separate residual oil of WW-II. After separation of residual oil, COD of resulted WW-II was measured. Results are presented in Table-11.

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TABLE - 11

25 ml WW-II (COD-1,20,000 mg/l) was treated with different Liquid Ion Exchangers at pH 2.

Liquid Ion exchanger	**Amount of L.I.E. in** gram	**COD value of effluent after the treatment** mg/l
1. Boramine - S	2.0	92,120
2. Boramine - S at pH 5	0.1	88,040
3. Boramine - T	0.1	80,000
4. Modified Boramine - S	0.1	96,170
5. Modified Boramine - S (pH 7)	0.1	101,760

The reference to Table - 11 shows that high pH and high dissolved solids of the effluent may not help the functioning of surfactant as de-emulsifying agent to act as effective de-emulsifying agent.

4. ADSORPTION ON ACTIVATED CARBON

Previous experiments suggest that with different optimization conditions the final COD value of effluent after the removal of organic oil is much higher. This effluent (WW-II) can not be disposed, hence some other tertiary treatments would be necessary to decrease COD value.

Preliminary experiments were carried out by using activated carbon as an adsorbent in a column. The amount of activated carbon and the concentration of solute were varied to optimize the condition of adsorption. Glass columns of 2.5 cm. internal diameter were used, upto 25 g carbon and in case of higher quantity columns of 5.5 cm. I.D. were used. Prior to each run carbon was immersed in distilled water for 24 hours to ensure complete weting of the carbon prior to operation [61].

The data of these experiments is recorded in Table - 12.

The reference to Table-12 shows that out of 3, 4 and 5 gms of activated carbon for 25 ml effluent, best results are obtained for 5 gms activated carbon (powder form) column (Sr.No. 1 to 6). The experiment number 7 is with granular carbon. The efficiency is less but working is smooth. Time taken to percolate is much higher in the case of powdered activated carbon. Especially when the experiment of carbon treatment was repeated for the scaled up experiment, the difficulties were faced. The effluent takes much more time due to high load of organics and inorganics in WW-II. This suggested that the load of at least organics should be reduced before adsorption on activated carbon and granulated activated carbon should be preferred over powdered activated carbon for adsorption.

The removal of organics from WW-II can be further achieved by solvents as these organics are soluble in the aqueous phase. To evaluate the efficiency of different solvents to remove organics from WW-II (to decrease COD value of WW-II) number of experiments were carried out to evaluate these parameters. Organic matters present in WW-II is difficult to remove as they are highly soluble. Quantity of activated carbon required to remove COD of about 90000 to 110000 mg/l is very high and thus the further reduction in COD becomes uneconomical. Therefore, step of solvent extraction with suitable solvent was tried to remove COD from WW-II. Different type of solvents were used. The data is summarized in Table-13.

TABLE-12

Adsorption on activated carbon.

Amount of WW-II (COD value) mg/l	Amount of activated carbon in gram.	Type of activated carbon	COD of the effluent after the treatment mg/l.
01. 25 ml (106000)	5.0	* AR grade	26,880
02. 25 ml + 25 ml distilled water (53000)	5.0	AR grade	10,000
03. 25 ml (100,000)	4.0	Extra grade	50,000
04. 25 ml (100,000)	4.0	OCS	85,000
05. 25 ml (100,000)	4.0	S - I	67,000
06. 25 ml (100,000)	3.0	Extra grade	47,200
07. 25 ml (100,000)	3.0	P - 15	44,862
08. 335 ml (100,000)	100.0	IC - 30/80	28,000

* AR Grade - Analytical Reagent Grade.

Specification of activated carbons used in this work is mentioned in Table-14.

5. EXTRACTION OF RESIDUAL ORGANICS FROM WW-II BY DIFFERENT SOLVENTS.

The reference to the Table-13 shows that many solvents are effective to reduce COD value i.e. they are capable of extracting residual organics from WW-II. However, LBP-T_1 is a byproduct of Caprolactam industry whose composition is given in Table-8. Due to this reason it was decided to use LBP as solvent for the extraction of residual organics from the WW-II. The extraction is about 50% of the COD which would reduce the load of effluent considerably for further treatment.

TABLE-13

Extraction of Residual organics from 25 ml WW-II by different solvents.

	Solvent	Amount in ml per extraction (a)	Initial COD mg/l	Final COD mg/l.
01.	Cyclohexanone	5	126,000	45,000
02.	Cyclohexane	5	126,000	66,000
03.	Butyl acetate	5	110,000	49,920
04.	Methyl isobutyl ketone	5	110,000	34,560
05.	Amyl alcohol	5	110,000	60,000
06.	Methyl isobutyl ketone	5	84,000	40,000
07.	Cyclohexanone	10	113,000	67,000(b)
08.	LBP-T_1	5	89,280	51,840
09.	LBP-T_1	10	113,000	76,000(b)

(a) in all the cases extraction was carried out twice by using 5 ml of solvent each time.

(b) In these experiments 50 ml effluent (WW-II) was taken for extraction, using 10 ml solvent for each time.

TABLE - 14

Specifications of activated Carbons.

Trade name of Activated Carbon	pH	Particle size	Moisture content %	Methylene blue value mg/g	Form	Bulk density g/cc	Iodine value	Iron Fe %
Extra Grade	9 - 10	90% through 200 mesh	5.0	160-165	Fine powder	-	-	-
S-I	8 - 8.5	90% through 200 mesh	5.0	60-70	Fine powder	-	-	-
OCS	6 - 7	90% through 200 mesh	5.0	80-85	Fine powder	-	-	-
P-15(This is chemically active)	-	-	-	-	Fine powder	-	-	-
IC-30/80	9 - 10	-	-	-	Granules	0.6±0.5	400-450±2½%	0.05
IC-16/40	9 - 10	-	-	-	Granules	0.6±0.5	400-450±2½%	-
AR grade of SD's Company	-	-	-	-	Fine powder	-	-	-
ICPM 8/30	9 -10	-	-	130-150	Granules	0.3±0.5	600-650±2½%	-

5.1 Increase in the efficiency of LBP solvents

Previous experiments suggested that use of LBP solvent is more feasible in the reduction of COD values of WW-II. Solvent LBP is the mixture of different components. It was thought to separate different fractions of LBP, and to determine efficiency of these fractions for the extraction of organics from WW-II.

For this purpose six fractions of LBP as reported in Table-15 were tried in a preliminary experiments. Preliminary experiments suggested that all the fractions distilling above 145°C exhibited properties as better solvent than LBP itself. Due to this reason LBP was distilled and two fractions were collected. Fraction-I was the 'cut' upto 145°C and fraction II was the residue left behind.

TABLE-15

Fractional Distillation of 100 ml LBP-T_1 to get six cuts.

Sr.No. of cut.	Temperature range °C	Quantity of fraction collected.
01.	95 - 110°C	11 ml
02.	110 - 130°C	15 ml
03.	130 - 145°C	25 ml
04.	145 - 149°C	23 ml
05.	149 - 150°C	11 ml
06.	150 - 154°C	15 ml
	Total:	100 ml

TABLE-16

Extraction of Residual organics from WW-II by LBP-I and LBP-II.

Amount of WW-II	Amount and type of solvent	Initial COD value mg/l	Final COD value mg/l
25	LBP - I 5 ml	100,000	80,000
25	LBP - II 5 ml	100,000	54,000
25	LBP - I 5 ml	113,000	89,000
25	LBP - II 5 ml	113,000	40,320
25	LBP - I 5 ml	125,000	70,000
25	LBP - II, 5 ml	125,000	48,000

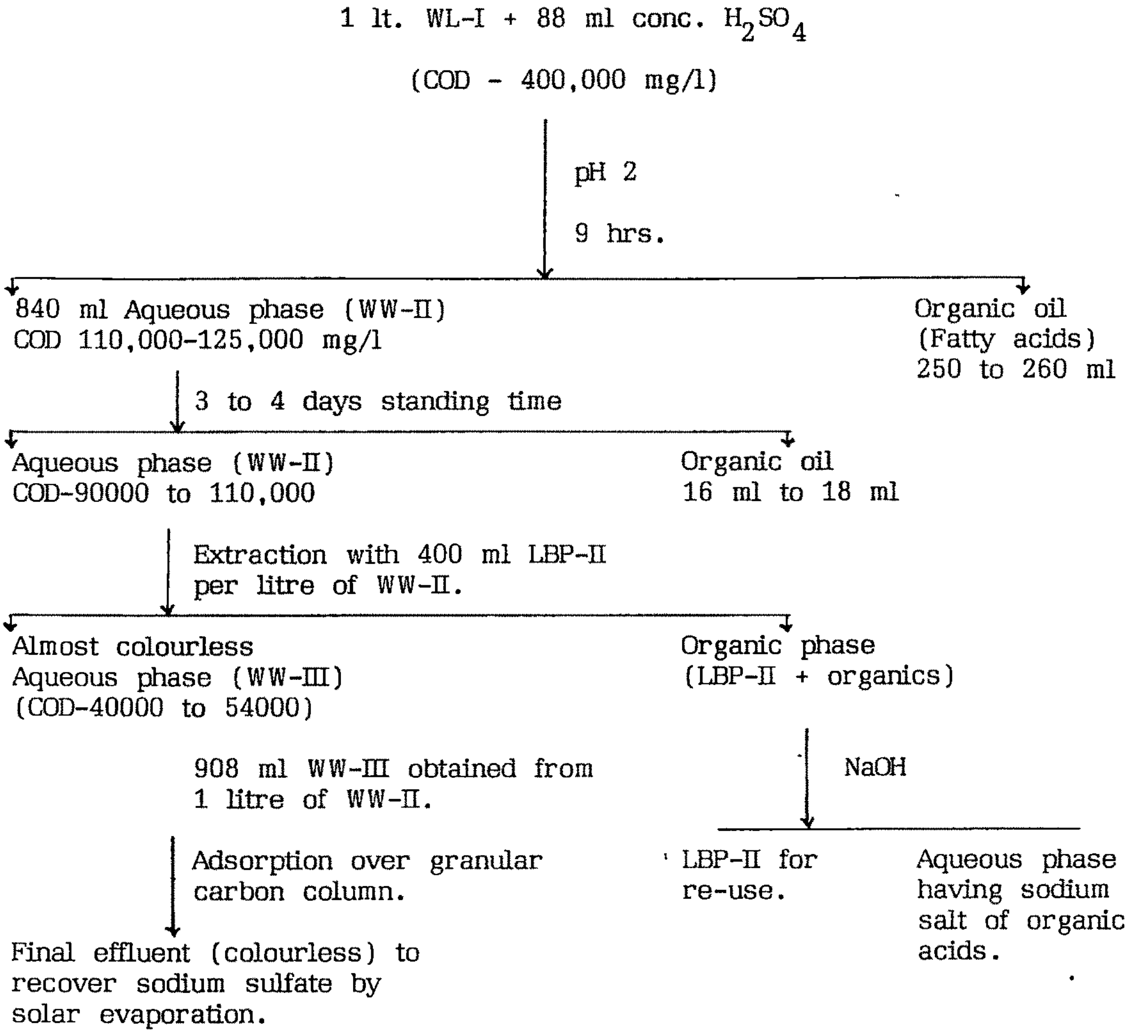
After the separation of two fractions, LBP-I and LBP-II were tried for the extraction of residual organics from WW-II.

The data of efficiency of both these fractions are given in Table-16.

The reference to Table-16 shows that efficiency of LBP-II in decreasing the COD of effluent is much higher compared to LBP-I. This might be higher solvation power of LBP-II compared to LBP-I. Due to this reason in other extraction LBP-II was used. This indicates that type of solvent plays its important role.

Based on all the experiments the information gathered was used for the reduction of COD from WL-I.

The strategy was followed as under.



1 lt. WL-I + 88 ml conc. H_2SO_4

(COD - 400,000 mg/l)

pH 2

9 hrs.

840 ml Aqueous phase (WW-II)
COD 110,000-125,000 mg/l

Organic oil
(Fatty acids)
250 to 260 ml

3 to 4 days standing time

Aqueous phase (WW-II)
COD-90000 to 110,000

Organic oil
16 ml to 18 ml

Extraction with 400 ml LBP-II per litre of WW-II.

Almost colourless
Aqueous phase (WW-III)
(COD-40000 to 54000)

Organic phase
(LBP-II + organics)

908 ml WW-III obtained from 1 litre of WW-II.

NaOH

Adsorption over granular carbon column.

LBP-II for re-use.

Aqueous phase having sodium salt of organic acids.

Final effluent (colourless) to recover sodium sulfate by solar evaporation.

5.2 Recycling of LBP-II

The efficiency of LBP-II in the removal of residual organics has been already discussed. These organics are mainly fatty acids. Recycling of solvent is important in any effluent treatment. LBP-II can be recycled by removing extracted organics by distilling them or by the chemical treatment. Distillation is not feasible due to two reasons. It involves higher cost of investment and operation. Moreover, it would not be easy to separate LBP-II components from residual extracted organics as the data of it is not determined. Due to these reasons regeneration by chemical method would be preferred.

As the residual organics are acids, alkali is the best to remove them from used LBP-II.

Sodium hydroxide solution was used to extract organic acids present in LBP-II. Two different concentrations of NaOH solutions were tried for the extraction. The regenerated LBP-II exhibits same efficiency as the original one which was extracted by 11.0% NaOH solution. (Table-17).

TABLE-17

Regeneration of used LBP-II by NaOH.

% of NaOH solution used to regenerate used LBP-II	Efficiency of regenerated LBP-II measured as COD value of effluent WW-III.
11 %	46,698
50 %	69,500

It is easy to separate organic and aqueous layers. This indicates that the regeneration of LBP-II by chemical method can be achieved.

6. ADSORPTION OF WW-III OVER GRANULAR ACTIVATED CARBON.

The COD value of WW-III is still high. The adsorption over granular activated carbon does remove residual organics as observed earlier. However, the method used before for decreasing the load of COD to a certain level could not be of much use.

In the present study column of fixed amount of granular carbon was kept constant. The WW-III with different dilution was passed through the carbon columns. The effluent obtained was analyzed for the presence of organics by estimating COD values.

The data, regarding the effluent is given in Table-18.

TABLE - 18

Sr. No.	Waste Water	Total Residue g/litre.	Total volatile solids. g/litre.	COD in mg/l
01.	WW-II at 2 pH	315.0 to 324	72.4 to 74.0	100,000 to 110,000
02.	WW-II at neutral pH (neutralized by NH_4OH)	321.6 to 325	81.4 to 83.0	100,000
03.	WW-III	290.0 to 300	-	45,000 to 64,000

TABLE - 19

Effect of concentration on the adsorption.

Sr. No.	Quantity of WW-III and added water.	Activated carbon IC-30/80 taken in column	Initial COD mg/l	Final COD in mg/l.
01.	250 ml	100 gm	64,832	2,300
02.	250 ml + 250 ml distilled water.	100 gm	32,416	2,800
03.	250 ml + 500 ml distilled water.	100 gm	21,610	2,276
04.	250 ml + 750 ml distilled water.	100 gm	16,208	1,560

Water has a high surface tension, and most solutes reduce its value; hence, the great majority of substances are positively adsorbed from aqueous solution by such an adsorbent as charcol. For most purposes, the empirical Freundlich isotherm is found to be adequate for adsorption from solution over a considerable range of concentrations.

$$a = kc^n$$

'a' is the amount of solute adsorbed by unit mass of adsorbent from a solution of concentration 'c'; 'k' and 'n' are constants for the given adsorbent and absorbate. Taking logarithms of above equation.

$$\log a = \log k + n \log c$$

So that log a against log c should give a linear plot.

The effect of concentration on the adsorption of organics was studied.

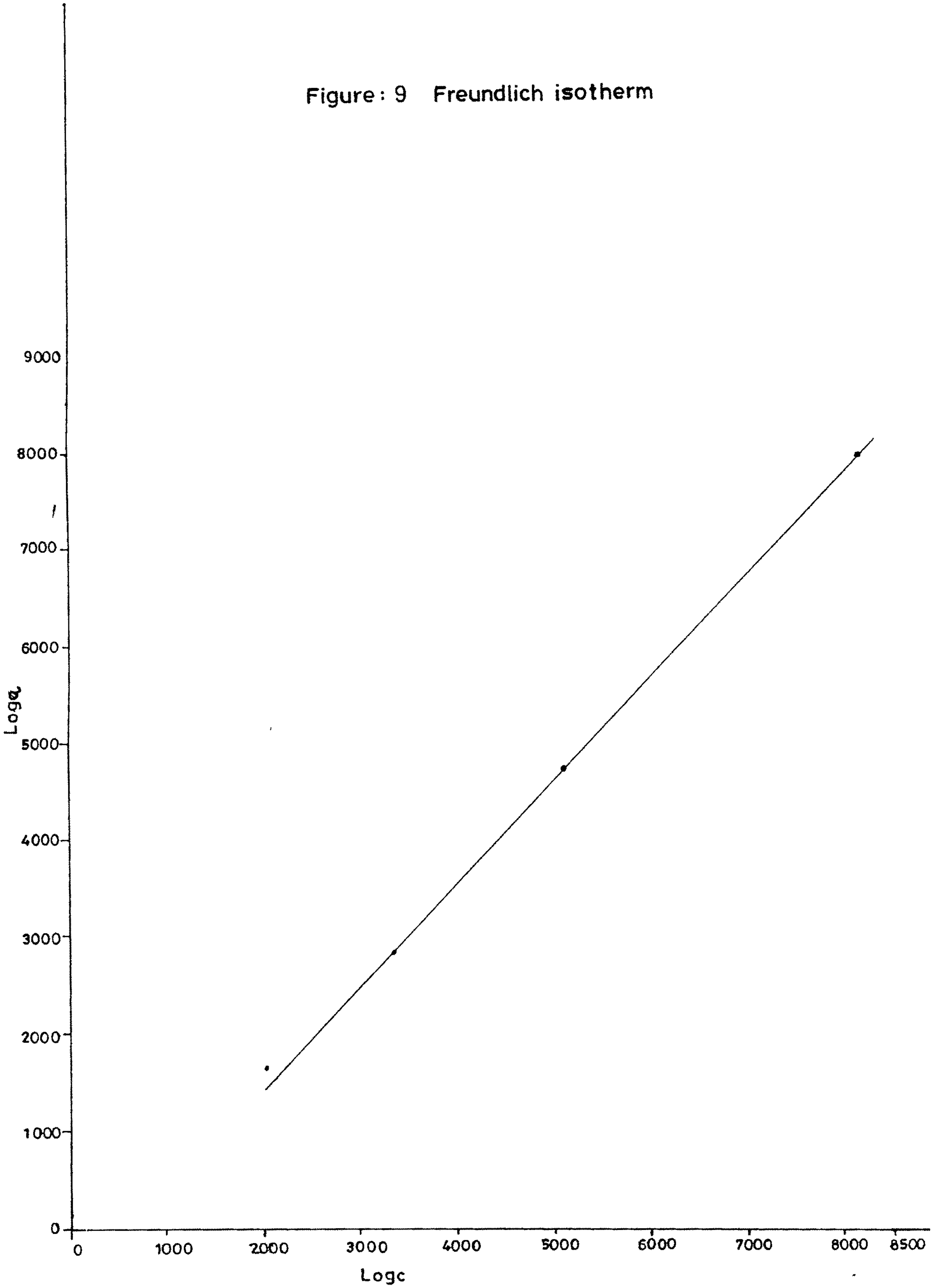


Figure: 9 Freundlich isotherm
Logq
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
Logc
0
1000
2000
3000
4000
5000
6000
7000
8000
8500

For this purpose different experiments were carried out as mentioned above. The data is recorded in Table-19.

The graph of log c versus log a (Fig.9) shows straight line. This indicates that the present system follows Freundlich isotherm.

More experiments were carried out on large scale by using 1 litre of WW-III and different amount of granulated carbon. The data is recorded in Table-20.

These results (Table-20) indicate that the COD value is decreased considerably.

The effluent with less COD value was passed through another column of activated granular carbon to study the efficiency of this additional treatment on the COD value of influent. The data on a scaled up quantity is recorded below.

Amount of final effluent in ml.	Amount of carbon IC-30/80 in gram	Initial COD mg/l.	Final COD mg/l
2000	80	3730	571
4000	160	3730	693

These results indicate that starting from 4,00,000 mg/l COD value one can achieve COD value of 500 mg/l through three unit processes.

(a) Acidification and separation of two layers.

(b) Extraction and separation of two layers.

(c) Adsorption on the granular carbon.

TABLE - 20

Adsorption of organics from WW-III on granular activated carbon.

Sr. No.	Type of carbon	Quantity of carbon in column	WW-III taken for treatment	Initial COD mg/l	COD of final effluent. mg/l
01.	IC - 16/40	100 gm	250 ml	60,100	8200
02.	IC - 30/80	50 gm	250 ml	64,000	33,000
03.	IC - 30/80	100 gm	250 ml	60,100	2,300
04.	IC - 30/80	150 gm	500 ml	60,100	5,400
05.	IC - 30/80	300 gm	1000 ml	60,100	4,018
06.	IC - 30/80	320 gm	1000 ml	60,100	4,312

7. RECOVERY OF SODIUM SULFATE (Na_2SO_4) FROM FINAL EFFLUENT

The aim of every research project in environmental study would be zero pollution. The final effluent obtained by the previous (treatment) stage has Na_2SO_4 in dissolved stage. Recovery of Na_2SO_4 can be made plausible by adopting proper methods.

It has been reported in the literature that cryogenic methods can be adopted for the recovery of Na_2SO_4 from such effluents. This work was conducted in USSR [62,76]. In our country 'Sun' is shining normally for the most of the time of the year. Utilization of solar energy is more economical for the recovery of Na_2SO_4 from final effluent.

The solar evaporation gives wet Na_2SO_4, which can easily be oven dried or can be dried directly in the sun when moisture content in the environment is very less.

The evaporation of 1 litre final effluent from a vessel of the size 27 cm diameter and 2 cm height was used for the evaporation. It takes about 24 hours to obtain a wet-cake (Na_2SO_4 with residual moisture). The recovery of Na_2SO_4 is quite good, 1 litre gives about 300 gms of Na_2SO_4. Results of recovery are tabulated in Table-21.

Sodium sulphate was recovered from both the types of final effluent. One having higher COD value compared to other due to second adsorption over granular activated carbon. The evaporation of water took place within 24 hours. This is reasonably more feasible approach. The solar evaporation can be enhanced further by using modern technology of solar energy. The evaporation of water is the only cost.

The Na_2SO_4 recovered is quite good in appearance. Small quantity of this material when treated with ethanol gives extra white Na_2SO_4. In most cases dull white or yellowish Na_2SO_4 is recovered.

The analysis of recovered Na_2SO_4 and final effluent for Na_2SO_4 are given in Table-22 and 23 respectively.

7.1 Proposed use of Recovered Na_2SO_4

The major use of sodium sulphate can be diluent in dyes, surfactants etc. [77]. Some experiments were carried out to exploit the utility value. The extent of foaming of surfactant was checked by adding recovered Na_2SO_4 in the surfactant solution. The hights of the foam observed in the blank, pure Na_2SO_4, and recovered Na_2SO_4, solution of surfactant does not appreciably change. At present Na_2SO_4 is being used in India as diluent in surfactant industries. Crystalline Na_2SO_4 has good demand in different industries. To fatch higher price one unit operation of crystallization and purification of Na_2SO_4 can be added.

TABLE-21

Recovery of Sodium sulfate from final effluent.

Amount of final effluent	COD in mg/l.	Amount of Na_2SO_4 recovered.
1 litre	571	290 gm
1 litre	3700	294 gm

TABLE-22

Analysis of Na_2SO_4 recovered from final effluent.

Sample	NH_3 %	SO_4'' * %	Na_2SO_4 %	$(NH_4)_2SO_4$ %	COD of final effluent mg/l
1	1.01	68.10	99.70	3.92	4,500
2	0.846	66.516	97.38	3.28	570

* SO_4'' due to Na_2SO_4, $(NH_4)_2SO_4$ and H_2SO_4.

TABLE-23

Analysis of final effluent (570 mg/l COD) for inorganic composition.

Sample	Free H_2SO_4 g	Sulfate as SO_4'' g	Sodium as Na^+ g	Nitrogen as N g
1.0 litre of final effluent	17.24	206.00	90.00	2.016

7.2 Potential use of final effluent in irrigation and fertilizer supplement

The final effluent with very little COD value (570 mg/l) can be used after due dilution for irrigation purposes. It contains about 10% of ammonium sulphate and 90% Na_2SO_4 if it is neutralized with ammonia. This effluent also contains traces of metals like Nickle and cobalt, which can act as microneutrients (catalysts from manufacturing processes). Initial experiments should be carried out on small area, and on different crops. If these experiments show promising results as expected then solar evaporation step may not be necessary for the recovery of sodium sulphate.

8. UTILIZATION OF FATTY ACIDS

The constituents of WL-I are given in Table-7. The recovered fatty acids are mainly mixture of mono and dicarboxylic acid. GSFC have tried to fractionate fatty acids and utilize them by preparing their esters for the purpose of fragrance or cosmetic agents. However, fractionation is expensive, moreover, the odour is very sensitive to little impurity. Only few of the acids can give odourous esters. The separation of dicarboxylic acid like adipic acid is also not efficient and economical by vacuum distillation. Because of all these reasons the main aspect is to find utility of separated mixed fatty acids. This is one of the vital problem to be solved for the feasibility of the present treatment.

For the utility of mixed fatty acids, in the present study two approaches are tried (a) to find utilization of mixed fatty acids and/or (b) fractionate fatty acids mainly in to two fractions, lower boiling (mainly monocarboxylic acids) acids and the residue (mainly dicarboxylic acid).

The utilization pattern is planned as under :

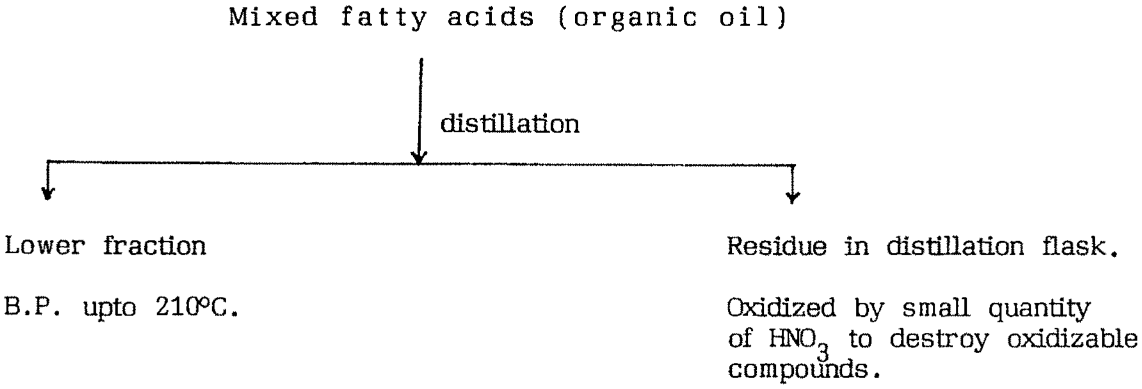
Mixed acids

(a) Polymer constituent for additives to oils.

(b) Modification of surfactants for quarternization of cationic surfactant.

(c) Conversion to amines

$$R - COOH \rightarrow R\text{-}CO\text{-}NH_2 \longrightarrow RCN \rightarrow R\text{-}CH_2NH_2$$



Mixed fatty acids (organic oil)

Lower fraction

B.P. upto 210°C.

Residue in distillation flask.

Oxidized by small quantity of HNO_3 to destroy oxidizable compounds.

Lower fraction : used for (a) to (c) application mentioned as above.

Residue : used for synthesis of polymer.

Alkyd type resin :

Alkyd resins are synthesised by using phthalic anhydride, glycerol and fatty acids. Unsaturated long chain fatty acids are important. However, small quantity of mixed fatty acids can be incorporated in the synthesis of alkyd resins. To exploit this possibility, number of experiments were carried out for the synthesis of alkyd type resins by incorporating different amount of mixed fatty acids (MF-acid).

8.1.1 Viscometric Study

Introduction

Many methods for measurement of viscosity are reported [63,64] but those which make use of the capillary are well suited for our purpose. It is a unique property that dilute polymer solution has much higher viscosity than that of pure solvent. This is because pressure of the dissolved macromolecules on the solution increases the energy dissipation in the linear flow over that for the pure solvent flow by the polymer segments. This large difference in viscosity, and various functions derived therefrom are usually measured to produce information about the nature of microstructure of the polymer under study. It will be proper to define viscosity functions which are being estimated for this purpose.

The ratio of the viscosity of a dilute polymer solution [η] to that of a pure solvent [η_0] of equal density and of equal hydrokinetic pressure is approximately equal to the polymer-solvent efflux-time ratio in the capillary viscometer. The latter ratio is designated as the relative viscosity [η_{rel}] or as the viscosity ratio [65].

(Dimensionless ratio) :

$$\eta_{rel} = \frac{\eta}{\eta_0}$$

Because η_{rel} approaches 1 and not zero as the solution becomes more dilute the relative viscosity obviously does not denote the polymer's ability to increase the viscosity of the dipersion medium. To compensate for this descrepancy, the relative viscosity is diminished by 1; a new term results, that is denominated as the specific viscosity (η_{sp}), increment due to all solute molecules. The specific viscosity relationship may be expressed by the equivalent form :

$$\eta_{sp} = (\eta - \eta_0)/\eta_0$$

Where η is the viscosity of the solution and η_0 that of the solvent.

The specific viscosity is not yet the intensive function derived because it increases with concentration. When the specific viscosity, divided by the concentration expressed in a new quantity known as the reduced viscosity (η_{red}), increment per unit solute concentration at given concentration or the viscosity number is obtained.

$$\eta_{red} = \eta_{sp}/c$$

Where c is concentration in g/dl.

Viscosity may also be expressed by logarithmic relation [66] termed either the inherent viscosity (η_{inh}) or the logarithmic viscosity number and be defined as $\ln \eta_{rel}/c$.

$$\eta_{inh} = \ln \eta_{rel}/c$$

Where c is concentration in gm/dl.

Usually the reduced and inherent viscosities have different values for a given concentration, the latter being lower. Neither of these terms is independent of concentration, but they are usually linear functions of concentration in dilute solutions which can be extrapolated to a common intercept as the concentration approaches zero [67]. The common limiting value of either of these functions in infinitely dilute solution is called the intrinsic viscosity (η), the limiting viscosity number.

$$[\eta] = \left|\frac{\eta_{sp}}{c}\right|_{c \to 0}$$

The intrinsic viscosity is the intensive property which permits the determination of molecular weight and the solution dimension of macromolecules.

The linear relationship between the reduced viscosity and the concentration is expressed by the Huggin's equation [68]. It is employed to estimate intrinsic viscosity.

$$\frac{\eta_{sp}}{c} = [\eta] + K' [\eta]^2 c$$

In the relation K' is Huggin's constant and is obtained by plotting η_{sp}/c versus C. The intercept yields $[\eta]$ and K' is calculated from the value of the slope which is equal to $K'[\eta]$.

Similarly Kraemer [66] relationship.

$$\frac{\ln \eta_{rel}}{c} = [\eta] - K'' [\eta]^2 c$$

can be applied to the experimental data and $[\eta]$ can be determined from the plot of

$$\frac{\ln \eta_{rel}}{c} \quad \text{vs} \quad C$$

The method known as one point methods are also used to calculate intrinsic viscosity [η] which avoids entirely the use of some constants such as K' and K". These one point methods have certain inbuilt limitations. They assume the linear behaviour between c and η_{sp}/c and/or $\ln \eta_{rel}$. Other modifications are also used which involve the constants. In the present study our main interest was the comparison of viscosity data within the similar polymeric systems, hence the following equation was used which is recommended for the one point method [69 A].

$$[\eta] = \frac{2\,(\eta_s - \ln \eta_{rel})^{1/2}}{c}$$

Where c is the concentration g/dl.

8.1.2 Experimental

The polymer samples have been characterized by measuring their intrinsic viscosity. Standardized suspended type Ubblehode viscometer was used for the measurement of viscosity of the polymer samples in suitable solvents. The viscometer was washed with chromic acid, rinsed several times with distilled water and finally with acetone and dried.

Solvents used for preparing the polymer solutions were purified by distillation before use. Solvents were filtered through G-3 tinted glass funnel. The solvent was carefully introduced in the clean viscometer held vertically in the thermostat and allowed to stand for ten minutes to attain constant temperature. The average flow time was measured by taking the three independent readings.

The required amount of well powdered and dried polymer was dissolved in suitable solvent. The clear solution was filtered through G-3 tinted glass funnel. The solution thus prepared was carefully introduced in a viscometer held vertically in thermostate. It was allowed to attain the thermostate temperature. The flow time was measured at least three times and the average flow time was noted. From the mean efflux time different viscosities were calculated and are summarized in Table - 25 and 30.

Similarly, viscosities of some of the polymers were measured by taking different concentrations of polymers at the same temperature.

8.2 Synthesis of alkyd type resin [69 B].

Alkyd resins with phthalic anhydride and DMI :

Appropriate amounts of phthalic anhydride, or DMI, glycerol and mixed fatty acids or its fraction were treated in a round bottom flask on sand bath, at 250-300°C for 15 to 30 minutes. The polymer formed is characterized by studying its properties.

Table - 24 summarized the amount of phthalic anhydride, glycerol and fatty acids used for the synthesis of alkyd resins. Number of variations were tried to optimize the reaction conditions.

The alkyd resin type polymers were evaluated for their physical properties like solubility in different solvent and measurement of solution viscosity, etc and are presented in Table - 25.

TABLE - 24

Polymers from phthalic anhydride / DMI

Polymer product Sr.No.	Phthalic anhydride in gram	Glycerol in gram.	Oil or fraction in gram	
01.	10	10	2.0	Lower fraction
02.	10	10	4.0	Lower fraction
03.	10	10	5.0	Lower fraction
04.	10	10	2.0	(Oxidized Residue)
05.	10	10	4.0	(Oxidized Residue)
06.	10	10	5.0	(Oxidized Residue)
07.	10	10	2.0	Organic oil
08.	10	10	4.0	Organic oil
	DMI*	Glycerol	M.F.acids	(Organic oil)
09.	10	8	10.0	
10.	10	10	5.0	
11.	10	10	-	
12.	Further polymerization of Polymer product Sr.No.5 under vacuum.			
13.	Further polymerization of Polymer product Sr.No.8 under vacuum.			

---

* DMI - Dimethyl isophthalate.

TABLE - 25

Viscosity at 30°C for 1% solutions of polymer in Dimethyl Formamide (DMF)

Polymer product No.	Mean time in seconds	Difference of time solution-solvent	$\eta_{relative}$	$\eta_{specific}$	$\eta_{inherent}$	$\eta_{reduced}$	$[\eta]$ Intrinsic viscosity
2	110	10	1.1	0.1	0.0953	0.1	0.0965
5	121	21	1.21	0.21	0.1906	0.21	0.195
8	119	19	1.19	0.19	0.1738	0.19	0.177
10	114	14	1.14	0.14	0.1310	0.14	0.133
11	110	10	1.1	0.1	0.0953	0.1	0.096
12	106	6	1.06	0.06	0.0582	0.06	0.0586
13	140	40	1.4	0.4	0.3364	0.4	0.352
DMF Solvent	100	-	-	-	-	-	--

8.3 Alkyd resins with Maleic acid

Few more polymers were prepared using maleic acid and glycerol. As summarized in Table - 26 appropriate amount of maleic acid, glycerol and mixed fatty acids or its fraction were heated in flask, with stirring till mixture produced solid mass.

TABLE - 26

Polymers from maleic acid.

Polymer product Sr.No.	Maleic acid gram	Glycerol gram	Mix. fatty acid/fraction gram
14	5	5	-
15	5	5	2.5 (Organic oil)
16	5	5	2.5 (oil fraction below 210°C)
17	5	5	2.5 (oxidized oil)

Table - 27 indicates that product Sr.No. 14, 15 and 16 are almost insoluble in different solvents while Sr.No. 17 is partly soluble in few solvents.

TABLE - 27

Solubility of polymers in different solvents.

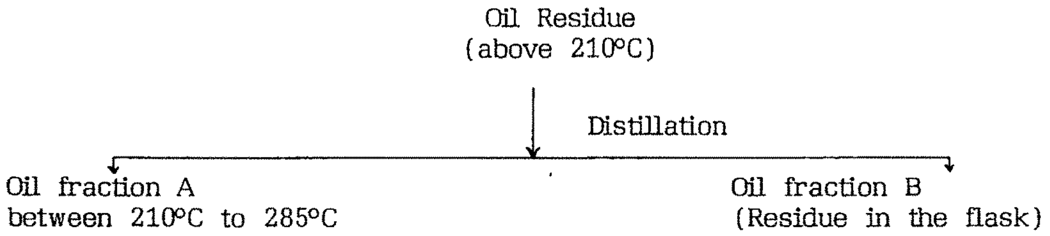
Polymer Product Sr.No.	Acetone	Dibutyl phthalate	DMF	Methyl alcohol
14	-	-	-	-
15	-	-	- (swellable)	-
16	-	-	- (swellable)	- (swellable)
17	±	-	±	-

+ means soluble.

- means insoluble.

8.4 Polymers with Diamines

Polymers were also prepared using oil fractions obtained by fractionation of Residue (above 210°C).



Synthesis of Polyamides

5 gm of above oil fractions (A or B) were taken and refluxed with Thinoyl chloride. After removal of excess of thionyl chloride, reaction mixtures were further treated with diamines in pyridine as catalyst, to obtain polymer as tabulated in Table - 28.

The polymers were purified with appropriate solvent. Their physical properties were studied. They were characterized by elemental analysis, viscosity and solubility etc. and are recorded in Table - 29 and 30 respectively.

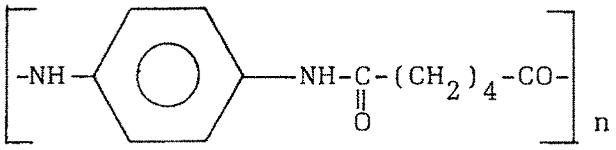
TABLE - 28

Polymers from Diamine and oil fraction

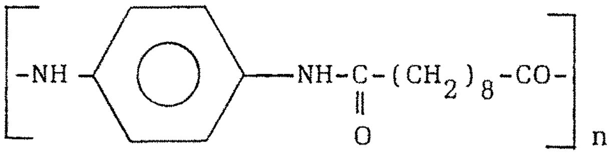
Polymer Product No.	Oil fraction	Diamines
18	A	P-phenylene diamine
19	B	p-phenylene diamine
20	A	1,6,diamino hexane
21	B	1,6,diamino hexane

Probable structures of Polymers Sr.No. 18 and 19 are presented as under: (Elemental analysis Table - 29)

Polymer No. 18 :



Polymer No. 19 :



IR spectra of Polymer Sr.No. 18 is presented in figure - 10 (Beckman Spectrophotometer Model IR - 4220).

TABLE - 29

Elemental Analysis of Polymer.

Polymer Product No.	Theoratical H%	Theoratical C%	Microanalysis H%	Microanalysis C%
18	6.4	65.9	6.36	65.49
19	8.0	69.8	5.54	60.74

TABLE - 30

Data of Polymers

Polymer Product Sr.No.	Solubility						Melting point °C	Viscosity				
	CH_3OH	Acetone	DMF	DMSO	N.M.P.	Conc. H_2SO_4		η_{rel}	η_{spe}	η_{red}	η_{inh}	$[\eta]$
18	+	±	+	+ on warming	+	+	170	1.053	0.0533	0.1066	0.1031	0.104
19	-	-	-	-	±	+ on warming	> 285					
20	+	+		+			85	1.019	0.192	0.0385	0.368	0.148
21	-	-		-			220 (d)					

(d)	decompose	DMSO	Dimethyl sulfoxide
+	Soluble	N.M.P.	N.Methyl,2-Pyrolidone
-	Insoluble		

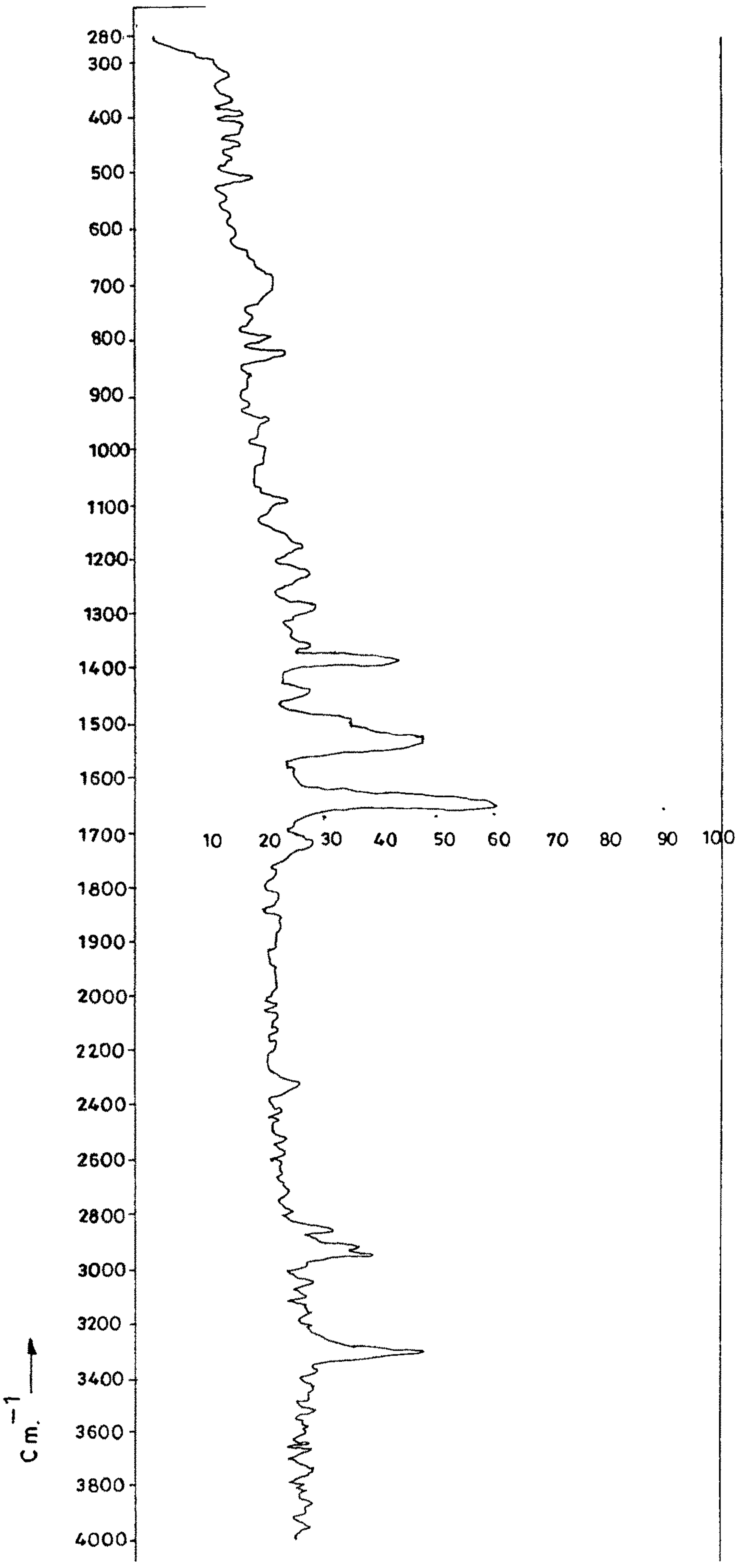


Figure:10 IR Spectra polymer. Sr. No. 18 (Table: 28)

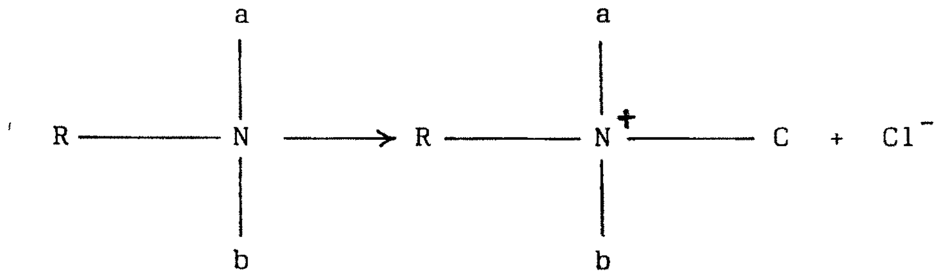
The solution viscosity measurements indicate that oligomeric compounds or polymers with lower degree of polymerization is visualised. However, when polymer product Sr.No.5 and 8 (Table-24) are heated under vacuum, higher degree of polymerization can be achieved as envisaged in polymer sample No.13 in the same Table.

These alkyd resins and polymers have opened up an avenue for application. Along with recovered fatty acids other higher fatty acids can be used in the synthesis of alkyd resins. Their properties can be evaluated for application in paints, oils and other related fields. The purpose of present investigation was to explore different possible avenues of utilization of mixed fatty acids. In the present work all the three variations are tried. Mixed fatty acids as such and fractionated constituents are used. It seems only two fraction of mixed fatty acids would be more potential for application. The fraction obtained upto 210°C, mainly will have monocarboxylic fatty acids whereas, the residue will be consisting of mainly dicarboxylic acids and oxy acids. This strategy should be exploited further on larger scale and results would definitely lead to utilization of mixed fatty acids.

8.5 Utilization of recovered fatty acids in the field of surfactants [69 C]

Synthesis of cationic surfactants involve mainly the following strategy.

Primary fatty amine is reacted further with alkyl halides with short alkyl chain to obtain secondary and tertiary amines and even for quarternization. The general structure of such surfactants is as under:



$$R - \overset{a}{\underset{b}{N}} \longrightarrow R - \overset{a}{\underset{b}{N^{+}}} - C + Cl^{-}$$

R - long alkyl chain

a, b and c are short alkyl chains like CH_3, C_2H_5 etc.

Primary amine can be reacted with mixed fatty acid chloride to obtain secondary and tertiary amines. In the sequence appeared primary or secondary amines can be further quarternized. Mixed fatty acids were fractionated. The fraction F-I as well as residue F-II are collected in the flask.

In the present work following procedure was adopted. (1) The acid was reacted with thionyl chloride and the fatty acid chloride was reacted with primary amine. (2) In the second procedure the mixed fatty acids were heated with primary amine. They will form secondary amine and even the salt of primary amine. Number of variations were tried in the synthesis of secondary and tertiary amines or modifications of primary amine. In most of the experiments Stearylamine (Boramine-S) or Boramine-T was taken as primary fatty amine.

The purpose of this approach is having greater significance in the utilization of mixed fatty acids. These fatty acids fractions can provide cheaper raw material in the synthesis of cationic surfactants from primary amine.

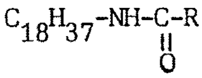
The data of such experiments of modification of primary amine are given in Table - 31.

These acylated primary amines or surfactants were tested for their efficiency. The efficiency of tertiary amines (B-DMS) was evaluated in our study reported in the next chapter for the removal of dyes and dyes-intermediate from the effluents.

Boramine - S   Primary amine $C_{18}H_{37}-NH_2$

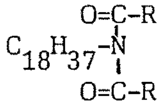
Modified :

(1) Boramine - S $\longrightarrow$ Secondary amine



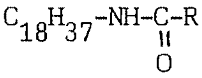
$C_{18}H_{37}-NH-\underset{\underset{O}{\|}}{C}-R$

(2) Boramine - S $\longrightarrow$ Tertiary amine

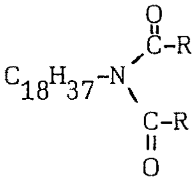


$C_{18}H_{37}-\underset{\underset{O=C-R}{|}}{\overset{\overset{O=C-R}{|}}{N}}$

(3) Boramine - S $\longrightarrow$ Mixture of secondary tertiary amines and the salts.



$C_{18}H_{37}-NH-\underset{\underset{O}{\|}}{C}-R$



$C_{18}H_{37}-N\begin{matrix} \diagup \overset{\overset{O}{\|}}{C}-R \\ \diagdown \underset{\underset{O}{\|}}{C}-R \end{matrix}$

$[C_{18}H_{37}-NH_3]^+[R-COO]^-$

TABLE - 31

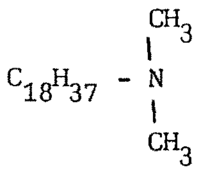
Reactants for modification of primary amines using oil fraction (below 210°C)

Modified amine product Sr.No.	Oil fraction g	Thionyl chloride ml	Boramine-S g	Boramine-T g
* 1.	3.7	-	5.0	-
* 2.	1.0	-	-	5.0
3.	3.7	8.0	5.0	-
4.	1.0	3.0	-	5.0
** 5.	3.7	-	5.0	-
** 6.	1.0	-	-	5.0

* Heated in water bath using air condenser.

** Heated on sand bath using air condenser.

The efficiency of all these products were tested as under: Measured quantity of coloured waste water was taken in a test tube and fixed quantity of these surfactants (mgs) was added. The most effective in removal of colour was the mixed amine obtained by heating primary amine and mixed fatty acids e.g. modified amine product No. 5 and 6 (Table-31). The efficiency is comparable with the Boramine-DMS, obtained commercially having structure,

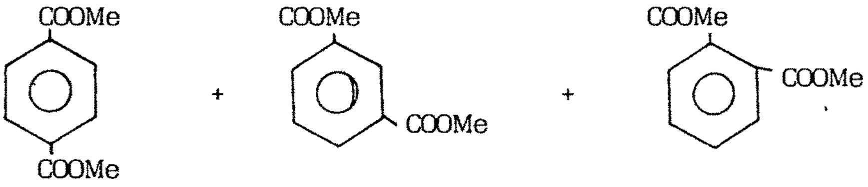


$$C_{18}H_{37} - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N}}$$

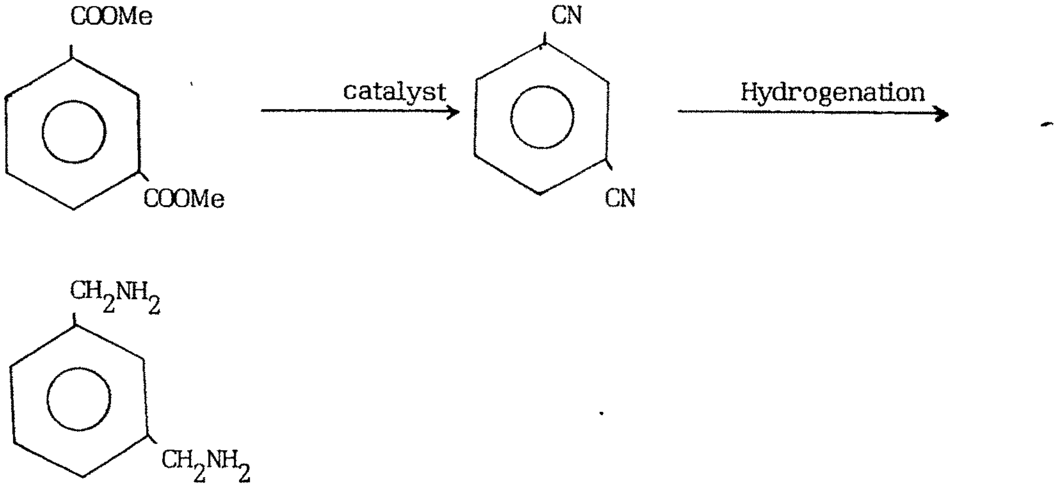
These results indicate that mixed fatty acids can find large scale use in the synthesis of cheaper cationic surfactants. Simple heating of primary fatty amine and mixed fatty acids gives a surfactant which is quite efficient as liquid ion exchanger.

8.6 Conversion of mixed fatty acids to mono and diamines

Mono and diamines are finding application in number of fields. They are used as corrosion inhibitors. They are widely used in epoxy resins etc. The recent patent report of obtaining mixed primary amines from DMI waste of petrochemical industry is very encouraging. DMI is the mixture of isomeric phthalates.

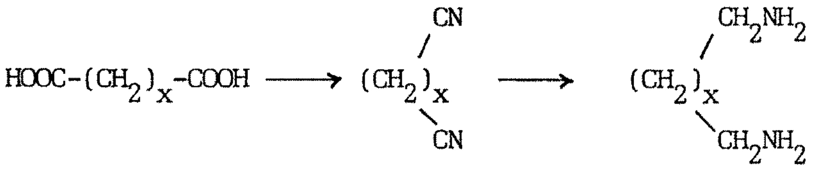


The conversion of this is carried out to primary amines as under



The strategy can prove highly useful for the utilization of recovered fatty acids.

$$R\text{-}COOH \longrightarrow R\text{-}CN \longrightarrow R\text{-}CH_2NH_2$$



$$HOOC\text{-}(CH_2)_x\text{-}COOH \longrightarrow (CH_2)_x\begin{matrix} / CN \\ \backslash CN \end{matrix} \longrightarrow (CH_2)_x\begin{matrix} / CH_2NH_2 \\ \backslash CH_2NH_2 \end{matrix}$$

Due to the limitations of time and the nature of work involved the route is not established in the laboratory. However, fatty amides were synthesised which could be dehydrated to nitrile. The strategy used for the conversion of DMI byproduct to mixed amines can be most appropriate for the utilization of mixed fatty acids.

8.7 Exploitation of Potential of mixed fatty acids; For the synthesis of "single cell protein".

The large amount of fatty acids can be a source for biotechnological approach to obtain energy and protein. It is known that fatty acids can be converted to methane and other hydrocarbons by microbes.

(1) Bacteria :

There are specific bacteria that produce methane from fatty acids. Two general mechanisms have been elucidated, one of these involves reduction of CO_2 and the other via methyl group of acetic acid.

Stadman and Barker [70] proposed reduction of CO_2 mechanism by methane bacteria.

$$2CH_3(CH_2)_2\ COOH + CO_2 + 2H_2O \longrightarrow CH_4 + 4CH_3COOH$$

$$2CH_3(CH_2)_3\ COOH + CO_2 + 2H_2O \longrightarrow CH_4 + 2CH_3.CH_2.COOH + 2CH_3COOH$$

The fatty acids products accumulated would be subjected to further fermentation to methane.

Bushwell and Sollo [71] proposed methane production via methyl group.

$$CH_3\ COOH \longrightarrow CH_4 + CO_2$$

$$4CH_3CH_2COOH + 2H_2O \longrightarrow 7CH_4 + 5CO_2$$

(2) Yeasts :

The alkane oxidation by yeast leads to the formation of corresponding primary alcohol, aldehyde and fatty acid. The fatty acid metabolism proceeds through β-oxidation and leads to the formation of C_2-compounds [72,73].

Gallo and Azoulay conducted studies using the yeast, Strain "Candida tropicolis" on n-alkanes, fatty acids and acetate. They calculated yield on growth substrate (Y_{sub}) and yield on ATP (Y_{ATP}). In the cells grown on alkane or fatty acids $Y_{(sub)}$ is very close to 1 i.e. 1 gram of metabolized substrate leads to the biosynthesis of 1 g of cellular matter. The generation time (T_g) has been measured during the growth on the different substrate and the T_g are of the same order of magnitude, (around 2.5 hours). The amount of ATP produced during n-alkanes, fatty acids or acetate metabolism in " Candida tropicolis" has been established from the P/O ratio measured on isolated mitochondiia, yield on substrate and carbon balance. The fact that Y_{ATP} is close to 4 with these three kinds of substrates, indicates that the 4 g of cells per mol. of ATP produced during the 'oxidation are not energy generating'.

Hunkova and Fencyl [74] investigated the actiion of different concentrations of fatty acids (from acetic acid to myristic acid) on cell growth, division, uptake of inorganic phosphate and substrate oxidation using the three yeast stains, saccharomyces cerevisiae, Candida utilis and Candida lipolytica. The former two yeasts were found to undergo an inhibition of growth, cell division and phosphate uptake at lower acid concentrations and to experience the inhibition of substrate oxidation at higher concentrations.

Joint work is going on between Applied Chemistry Department, Faculty of Technology and Engineering and Microbiological laboratory of Indian Institute of Petroleum on the biotechnological problems. Main work is on the bioconversion of organics by using yeast. It was thought worth to initiate some work on the bioconversion of mixed fatty acids to useful products. An U.S.Patent [75] has mentioned the production of cellular protein from the waste liquids obtained in the cyclohexane oxidation. They had used microoganisms of the family of pseudomonadaceae.

In the present study the use was made of yeast culture IIP-4 belonging to the species "Candida tropicalis" on the fatty acids developed in the above Microbiological laboratory. Yeast strain IIP-4 which has been found to grow on n-paraffinic hydrocarbons C_{14}-C_{18} with a specific growth rate 0.38 hr^{-1} and on molasses with specific growth rate 0.96 hr^{-1} shows growth at the initial stage. However, later on the growth is hindered due to number of problems. One of the reasons that could be attributed is improper mixing of these fatty acids with the nutrient medium containing yeast culture. With better emulsifying systems using emulsifiers or with ultrasonic sonicator and with suitable adaptation, technique in developing a yeast stain which can cultivate better and grow on fatty acids, it is hoped to succeed in producing single cell protein from recovered fatty acids.

This attempt for utilization of recovered fatty acids has great potential and given proper attention and time frame, can lead to the major utilization of fatty acid waste of caprolactam plant.

9. CROSS CHECKING AND VARIFICATION OF COD RESULTS

9.1 The results reported earlier (COD etc.) were also monitored by GC Chromatography. After establishing optimum conditions one batch was simultaneously monitored by GC. The COD data are consistent with GC analysis. The chromatograms obtained for WL-I, WW-II, WW-III and final effluent are recorded in Fig. 11 to 14 respectively. The COD data for each of these are given below.

Waste water	**COD values mg/l**
WL-I	4,20,000
WW-II	1,10,000
WW-III	54,000
Fianl effluent	570

Comparison of COD data with the chromatograph further confirms the results that organics present in WL-I are effectively removed.

Chromatograms were also taken for LBP-II before extraction and after extraction of WW-II. Difference in these two figures 15 and 16 clearly indicates the extraction of organics from WW-II by LBP-II. Retention time and area % of various peaks of these chromatograms i.e. Figure 11, 12, 13, 14, 15 and 16 are presented in Tables - 32, 33, 34, 35, 36, and 37 respectively.

9.2 TC and TOC Analysis

COD values were further cross checked by TC/TOC analysis. The TC/TOC analysis also indicate the steep drop from WL-I to final effluent. The trend is supporting the results of COD experiments. Results are presented in Table - 38 and 39.

9.3 BOD value of WW-II

Analysis of BOD for samples of WW-II having COD 1,36,000 and 2,00,000 mg/lt were also carried out and values of BOD obtained were 70940 and 1,11,000 mg/lt respectively.

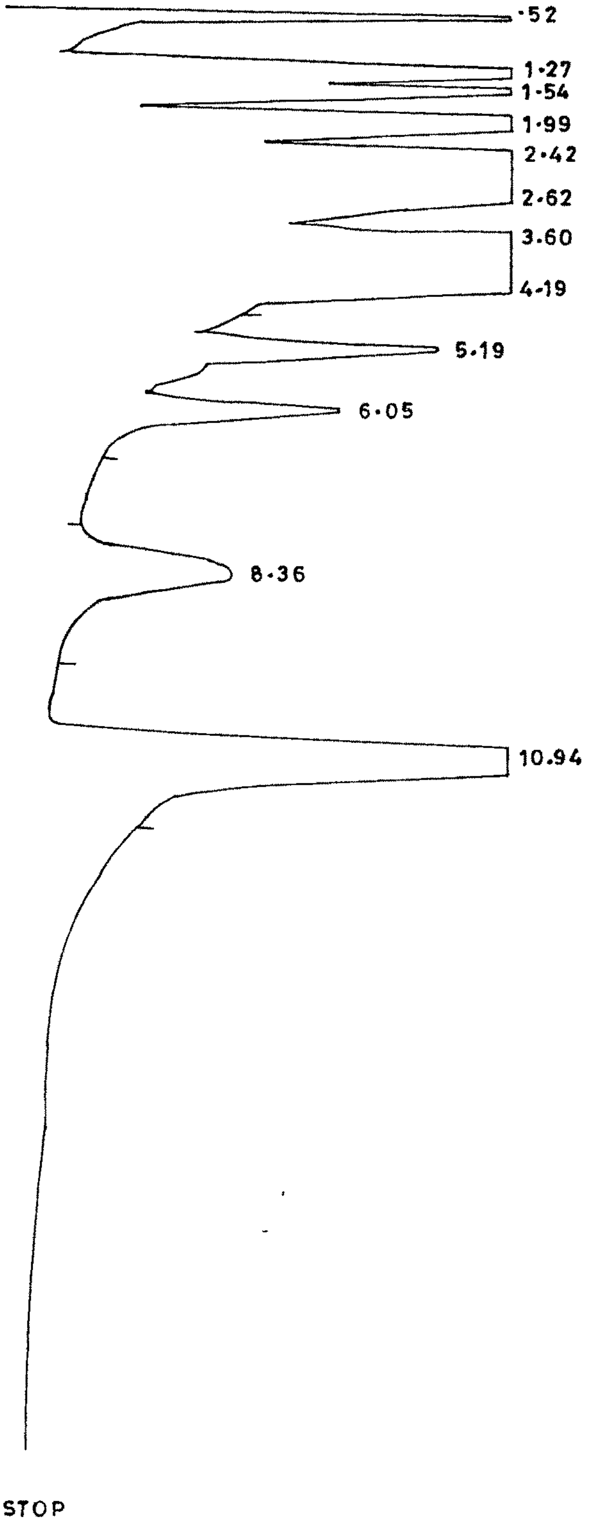


Figure-11 CHROMATOGRAM OF WL-I

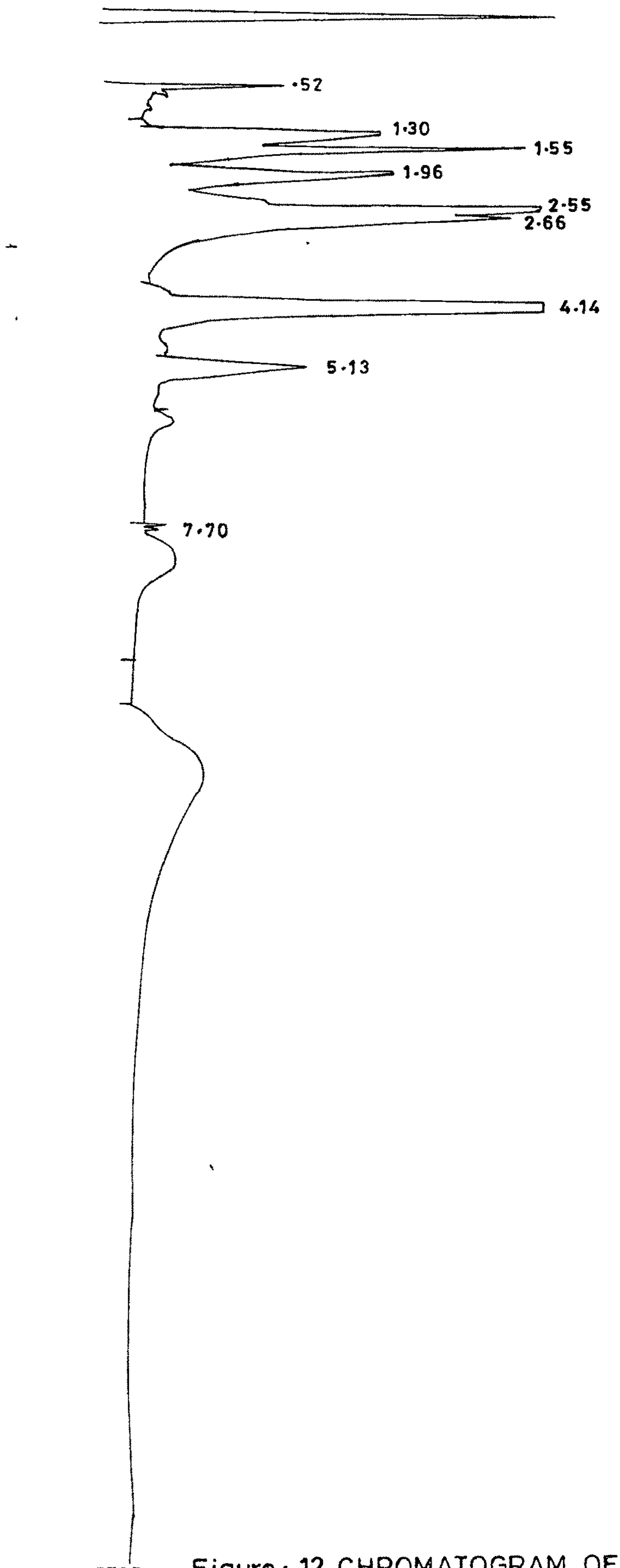


Figure :-12 CHROMATOGRAM OF WW-II

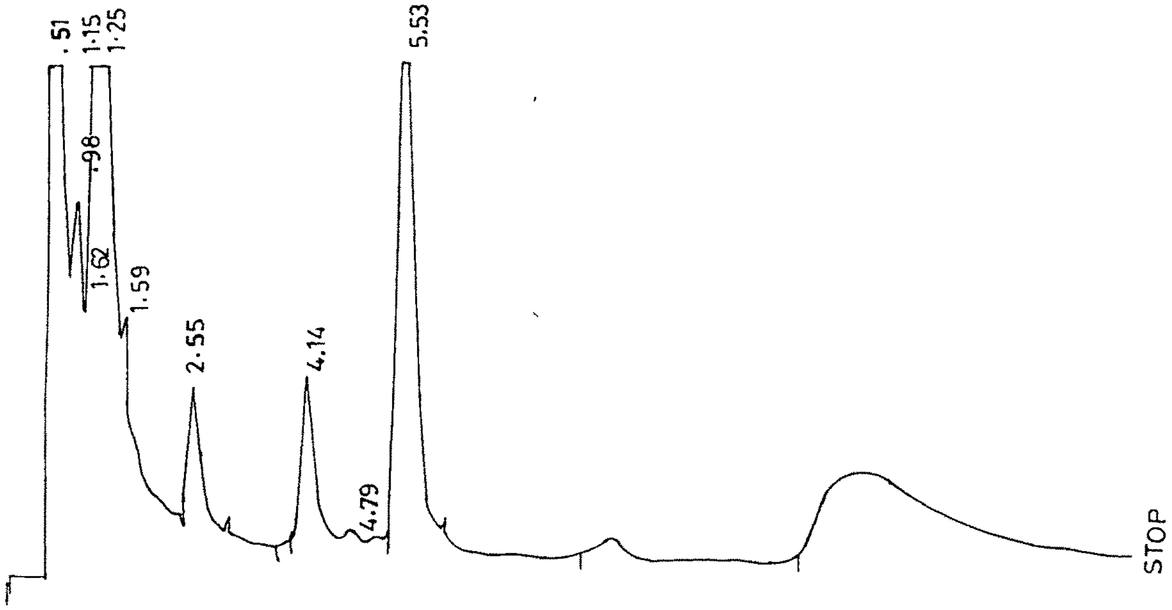


FIGURE:- 13 CHROMATOGRAM OF WW-III

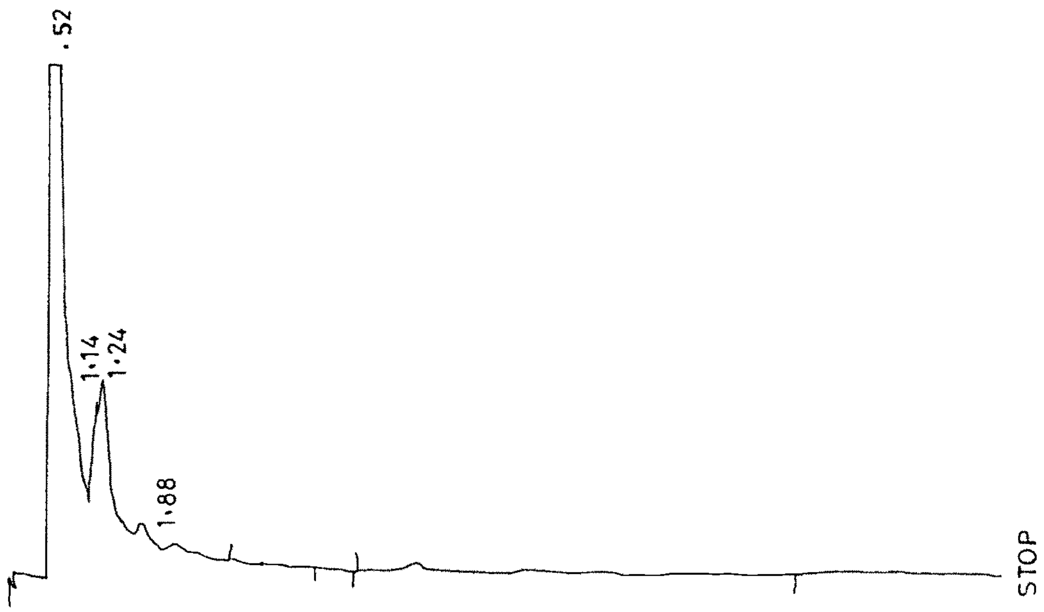


FIGURE:-14 CHROMATOGRAM OF FINAL EFFLUENT

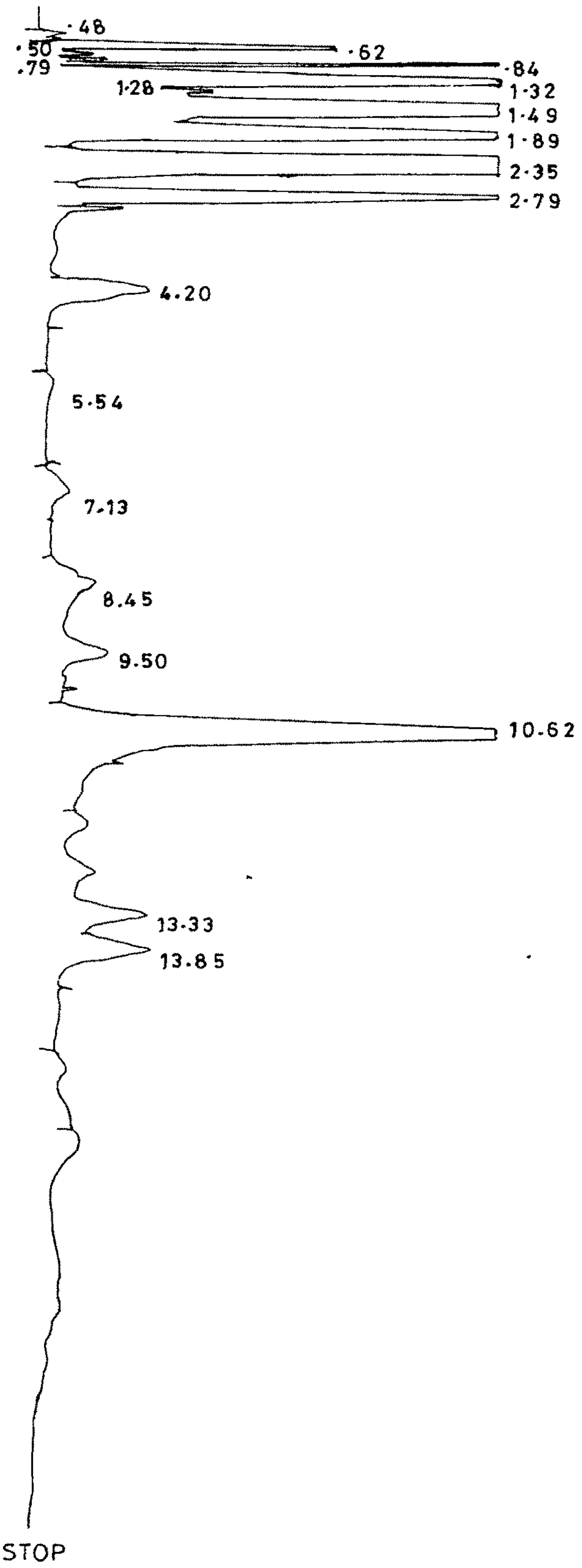


FIGURE:-15. CHROMATOGRAM OF LBP-II

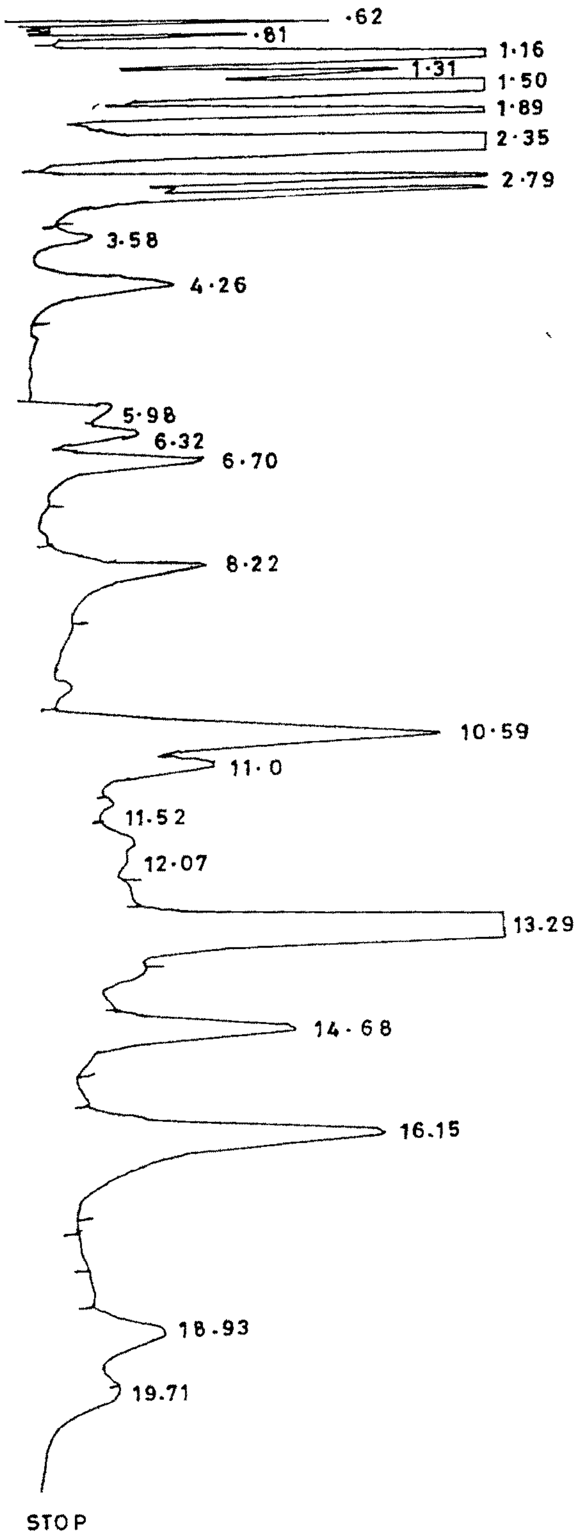


FIGURE :- 16 CHROMATOGRAM OF LBP-II AFTER EXTRACTION

TABLE - 32

Area % RT	Area	Type	AR/HT	Area %
0.52	30,845	D PB	0.011	0.847
1.27	166,840	PV	0.177	4.581
1.54	53,907	VB	0.068	1.480
1.99	315,430	PP	0.190	8.661
2.42	38,796	PV	0.099	1.065
2.62	1,604,800	VB	0.197	44.062
3.60	459,010	BV	0.228	12.603
4.19	428,000	VB	0.234	11.751
5.19	66,132	BP	0.280	1.816
6.05	50,064	PB	0.259	1.375
8.36	99,035	BB	0.632	2.719
10.94	329,880	PB	0.512	9.041

Total Area = 3642100

Mul Factor = 1.0000E + 00

Ref. Figure : 11

TABLE - 33

Area % RT	Area	Type	AR/HT	Area %
0.52	772	D PB	0.006	0.135
1.30	52,455	BV	0.200	9.154
1.55	59,825	VV	0.141	10.440
1.96	61,395	VV	0.224	10.714
2.55	65,646	VV	0.163	14.946
2.66	100,680	VB	0.249	17.559
4.14	175,350	PB	0.202	30.601
5.13	36,478	BP	0.223	6.366
7.70	492	PB	0.018	0.086

Total Area =573,030

Mul Factor = 1.0000E + 00

Ref. Figure : 12

TABLE - 34

Area % RT	Area	Type	AR/HT	Area %
0.51	122,090	D PB	0.010	22.944
0.90	7,305	BP	0.092	1.373
1.02	428	PV	0.032	0.080
1.15	79,490	VV	0.092	14.938
1.25	125,310	VV	0.149	23.549
1.59	1,550	D VB	0.018	0.291
2.55	23,768	BB	0.190	4.467
4.14	35,482	BV	0.230	6.668
4.79	2,069	VB	0.182	0.389
5.53	134,630	PB	0.259	25.300

Total Area = 532120
Mul Factor = 1.0000 E + 00
Ref. Figure : 13.

TABLE - 35

Area % RT	Area	Type	AR/HT	Area %
0.52	53,705	D PB	0.005	67.454
1.14	6,936	BV	0.076	8.712
1.24	16,872	VP	0.146	21.191
1.80	2,104	PP	0.156	2.643

Total Area = 79612
Mul Factor = 1.0000 E + 00
Ref. Figure : 14

TABLE - 36

Area % RT	Area	Type	AR/HT	Area %
0.48	3,617	PB	0.033	0.021
0.59	9,876	PV	0.025	0.057
0.63	38,034	VV	0.033	0.220
0.70	3,953	VP	0.033	0.023
0.75	636	PV	0.023	0.004
0.84	80,317	VB	0.043	0.465
1.08	301,250	PV	0.106	1.745
1.14	98,461	D VV	0.058	0.570
1.28	18,713	VV	0.055	0.108
1.49	4,805,200	VB	0.089	27.826
1.89	635,540	BB	0.095	3.680
2.35	1.0723 E+07	PB	0.135	62.098
2.79	260,700	BB	0.121	1.510
4.20	25,417	BB	0.265	0.147
5.54	3,224	PB	0.304	0.019
7.13	7,656	BV	0.325	0.044
8.45	21,259	PV	0.466	0.123
9.50	14,668	VB	0.298	0.085
10.62	170,280	PB	0.270	0.986
13.33	21,106	BV	0.269	0.122
13.85	25,232	VB	0.290	0.146

Total Area = 1.7268 E + 07

Mul Factor = 1.0000 E + 00

Ref. Figure: 15

TABLE - 37

Area % RT	Area	Type	AR/HT	Area %
0.49	729	PB	0.026	0.005
0.62	36,571	PV	0.033	0.227
0.69	2,350	VV	0.029	0.015
0.74	2,230	VV	0.029	0.014
0.81	33,557	VB	0.042	0.208
1.06	249,050	PV	0.088	1.545
1.14	226,350	VV	0.072	1.405
1.31	119,350	VV	0.107	0.741
1.50	3,095,400	VB	0.083	19.208
1.89	565,010	BP	0.097	3.506
2.35	1.0373 E+07	PB	0.134	64.370
2.79	253,520	BV	0.123	1.573
2.96	67,203	VB	0.120	0.417
3.58	7,674	BP	0.172	0.048
4.26	35,395	PB	0.256	0.220
5.98	18,910	BV	0.234	0.117
6.32	24,662	VV	0.247	0.153
6.70	40,347	VB	0.251	0.250
8.22	43,672	BB	0.300	0.271
10.59	120,090	PV	0.344	0.745
11.00	37,961	VV	0.288	0.236
11.52	5,065	VV	0.243	0.031
12.07	10,649	VB	0.359	0.066
13.29	492,330	BB	0.262	3.055
14.68	56,836	BB	0.301	0.353
16.15	131,300	BB	0.456	0.815
18.93	40,442	BV	0.505	0.251
19.71	25,065	VP	0.481	0.156

Total Area = 1.6115 E + 07
Mul Factor = 1.0000 E + 00
Ref. Figure : 16

TABLE - 38

Analysis of Total Carbon and Total Organic Carbon using Dohrmann Carbon Analyser.

Waste water Sample	COD mg/l	TC mg/l	TOC mg/l
WL - I	400,000	143,500	143,200
WW - II	113,000	43,700	40,520
WW - III	58,800	25,000	19,150
Final effluent	570	628	512

TABLE - 39

Analysis of total organic Carbon using TOC Analyser, Beckman USA Model - 915 - B.

Waste water sample	COD mg/l	TOC mg/l
WL - I	420,000	170,000
WW - II	115,000	43,000
WW - III	70,430	32,000
Final effluent	570	310
Final effluent	4,500	2,000

10. SUMMARY AND CONCLUSIONS

Number of variation have been mentioned in different patents for the treatment of waste liquor from the Caprolactam plant [78-89]. The common features for the most of the processes are acidification, separation of two layers (organic and aqueous), recovery of salt from aqueous layer.

Variation in acidification involves mixture of H_2SO_4-H_3PO_4, HNO_3, or acetic acid [90-92].

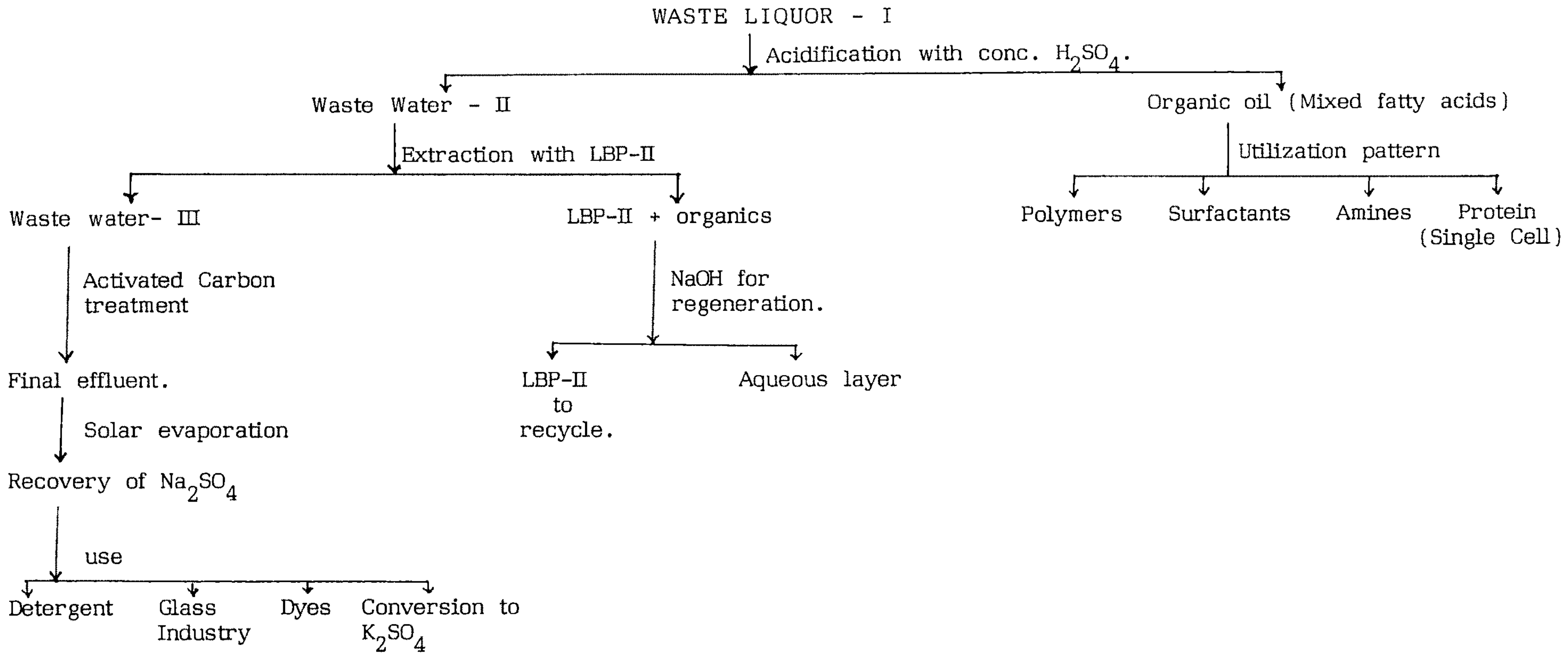
Extraction of organics (total) or residual after the separation of organic layer is carried out by using different solvents like C_7H_{14}, $C_{10}H_{22}$, Kerosene alongwith $(BuO)_3PO_4$, chlorinated hydrocarbons and cyclohexane or ketone.

The recovery of sodium sulfate is carried out by distillation of water under vacuum or by evaporation at higher temperature. In case of acidification by HNO_3 and acetic acid, $NaNO_3$ and sodium acetate are recovered respectively [62,76,77,92,93]. Some of the strategies for the treatment of waste water of caprolactam are based on the high temperature high pressure oxidation of organics [93,94].

The over view of literature survey indicates that the approaches mentioned in the literature can not be adopted for the country like ours where resources are to be used carefully.

The present strategy is developed keeping in view of literature survey and with indigenous approach.

The strategy of removal, recovery of organics and their utilization, from waste water is discussed in the foregoing section. Out of all the host of experiments final picture emerges as under.


WASTE LIQUOR - I
Acidification with conc. H_2SO_4.
Waste Water - II
Organic oil (Mixed fatty acids)
Extraction with LBP-II
Utilization pattern
Waste water- III
LBP-II + organics
Polymers
Surfactants
Amines
Protein (Single Cell)
Activated Carbon treatment
NaOH for regeneration.
Final effluent.
LBP-II to recycle.
Aqueous layer
Solar evaporation
Recovery of Na_2SO_4
use
Detergent
Glass Industry
Dyes
Conversion to K_2SO_4

10.1 Economical aspects and feasibility of the present method:

Economical aspects are mentioned hereunder taking the base for treatment of 10,000 litres WL-I.

(A) Requirement of materials for treatment

Conc. H_2SO_4	LBP-II (Regenerable)	Granular activated carbon (Regenerable)	NaOH for the regeneration of LBP-II
880 Lts.	3360 Lts.	2288 Kgs.	325 Kgs.

(B) Recovery of materials

Fatty acids	Sodium sulfate
2500 Lts.	2436 Kgs.

(C) Saving of materials

Waste Liquor-II	Extra Fuel
1770 Kgs.	500 Kgs.

The reference to above strategy and the data clearly indicates the economical aspects of the present approach. Over and above this, it provides an opportunity to "Zero Pollution" to the Caprolactam industry which is otherwise thought as an "Eutopia".

10.2 The photograph 'CPW' represents the samples bottled, of different stages of the effluent treatment.

Bottle No. 1 to 4 represents WL-I, WW-II, WW-III and final effluent respectively.

Bottle No. 5 represents the recovered organic oil (mixed fatty acids).

Bottle No. 6 and 7 represents samples of recovered Na_2SO_4 of different purity.

Bottle No. 8 and 9 represents LBP-II and LBP-II with extracted pollutants respectively.

Bottle No. 10 contains WL-II used for incineration of WL-I along with fuel oil.

CPW

Bottle No : 01. : WL-I

02. : WW-II

03. : WW-III

04. : Final effluent

05. : Organic oil (Mixed fatty acids)

06. : Na_2SO_4

07. : Na_2SO_4 (purified by alcohol washings)

08. : LBP - II

09. : LBP-II with extracted organics.

10. : WL-II