iJRASET
International Journal For Research in Applied Science and Engineering Technology



INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 7 **Issue:** X **Month of publication:** October 2019

DOI: http://doi.org/10.22214/ijraset.2019.10015

www.ijraset.com

Call: 08813907089 | E-mail ID: ijraset@gmail.com

International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 7.177
Volume 7 Issue X, Oct 2019- Available at www.ijraset.com

Reactive Extraction of Caproic Acid using Mixed Tertiary Extractant in Non-toxic Diluents

Praneet Mishra[1], Kavita Srivastava[2], Deepak Srivastava[3], A K Rathore[1]
[1, 4]*Department of Chemical Engineering, School of Chemical Tech., H.B.T.U, Kanpur (UP), India*
[2]*Department of Chemistry, V.S.S.D. College, Kanpur (UP), India*
[3]*Department of Plastic Technology, School of Chemical Tech., H.B.T.U, Kanpur (UP), India*

Abstract: ***The extraction of caproic acid from dilute aqueous stream is of great acceptance due to its high market demand and environmental aspect. The present study deals with the reactive extraction of caproic acid of initial concentration (0.01-0.057 mol/lit) using mixed tertiary amine extractant (tri-n-dodecylamine, TDA, tri-n-hexylamine, THA, tri-n-propylamine, TPA, tri-n-octylamine, TOA) in non-toxic diluents (jatropha oil biodiesel and soybean oil biodiesel) from its dilute aqueous solution. Different combination of mixed extractant and biodiesels were studied in order to reduce the toxicity. All the results of extraction experiments were presented in the form of distribution coefficient (K_D) and degree of extraction (% E). Both physical and chemical extraction were performed at T=302 K ± 1K to get maximum outcome of distribution coefficient and extraction efficiency. For physical extraction, the values of distribution coefficient and degree of extraction were obtained in the range of 0.57 to 4.26 and 35.92 to 80.98 for jatropha oil similarly, 0.59 to 4.33 and 37 to 81.23 for soybean oil. For chemical extraction, the values of distribution coefficient and degree of extraction were obtained in the range of 6.63 to 31.76 and 86.9 to 96.95 for jatropha oil similarly, 6.56 to 33.55 and 86.8 to 97.11 for soybean oil. In this research work it was found that the combination of mixed tertiary amine with soybean oil biodiesel is better than jatropha oil biodiesel in order to obtained maximum distribution coefficient (K_D) and extraction efficiency (% E). The problem of toxicity was found to be reducing by the use of non-toxic diluents with the mixed extractant.***

Keywords: Reactive extraction, caproic acid, amine extractant, non-toxic diluents, toxicity.

I. INTRODUCTION

Reactive extraction is one of the promising separation methods for the recovery of valuable carboxylic acids over the other separation methods such as distillation, Electrodialysis, solvent extraction and conventional precipitation process. The extraction of acids from the fermentation broth suffers the toxicity problem and the obtained products from broth mostly have the low concentration. Reactive extraction is an effective alternative method with the combination of suitable non-toxic diluents for the extraction of carboxylic acids [1-5]. Caproic acid, commonly known as haxanoic acid $\{CH_3(CH_2)_4COOH\}$ belongs to the member of fatty acid group and is found in fats and oils of animal [6]. Caproic acid is mostly used in pharmaceuticals, lubrication, perfumes, dye, plastics etc. It is light yellowish transparent oily liquid with pungent smell. At present, caproic acid is commercially produced by carbonylation of ethylene with CO and water or direct oxidation of hydrocarbons. Fermentation route is also available which is ecofriendly and regenerative method for the extraction of caproic acid [7-8]. Reactive extraction involves the combination if reaction and separation in a single unit. It involves both physical and chemical extraction with or without use of extractant. In reactive extraction process organic solvents like alcohols and ketone offer low distribution coefficient. Extractant play an important role to enhance the distribution coefficient of acid as the result degree of extraction of acid get increases. Therefore, the selection of diluents along with the suitable extractant is a key factor for the reactive extraction process. There is a lot of work done on the extraction of caproic acid using TBP as an extractant [9-13] but very few works has been done using amine extractant or mixed tertiary amine extractant.

II. EXPERIMENTAL SECTIONS

A. Materials

Caproic acid, light yellowish liquid (mass fraction 99%, M Wt 116.2) was procured from SRL Pvt. Ltd. India. Mixed extractant TOA (mass fraction 98%, M Wt 353.67), THA (mass fraction 96%, M Wt 269.51), TPA (mass fraction 98%, M Wt 143.27) were purchased from Sigma-Aldrich and TDA (mass fraction 85%, M Wt 522) was purchased from TCI. Non-toxic diluents (jatropha oil, soybean oil) supplied from local vendor and were used without pretreatment. Deoinized water was used for the preparation of aqueous solution of various concentration of caproic acid solution. NaOH used for the titration was procured from SD Fine-chem. Ltd., India. Oxalic acid (mass fraction 99.8%) was obtained from SD Fine-chem. Ltd., India used for the standardization of NaOH

©IJRASET: All Rights are Reserved

solution. Phenolphthalein (p^H range of 8.2 to 9.8) used as an indicator was obtained from Fine-chem. Ltd., India. Initial aqueous phase concentration of caproic acid was taken in the range of (0.01 to 0.057) mol/l and concentration of mixed extractant (20% v/v).

B. Methods

Extraction experiments (physical and chemical) were performed in a temperature controlled orbital shaker incubator (Shivam Instruments Pvt. Ltd., India) at a constant temperature (303K). Equal volume of aqueous phase and organic phase (each 10 ml) were taken in a 250 ml conical flask were kept in orbital shaker incubator for exactly 4 hours. This time could be assumed as the sufficient time for attaining the equilibrium. After that the mixture was allowed to settle for the separation of aqueous and organic phases. The mixture was kept in the centrifuge equipment (Remi Equipment Pvt. Ltd., India) for 10 to 15 minutes at 1400 to 1500 rpm. Separating phases could be easily seen and lower phase (aqueous) was taken for the analysis. The final aqueous phase concentration was determined by titration with NaOH. The results obtained from above method were assumed to be accurate when NaOH was prepared fresh every time before titration was to be performed. Acid in the organic phase was simply determined by the mass balance. Experiments were repeated twice in order to get more accuracy and consistency and found in the limit of ±2%.

Since caproic acid is a monocarboxylic acid therefore, the acid content present in the aqueous phase was calculated by equation (E-1), apart from that acid content present in organic phase was determined by the mass balance, the distribution coefficient of acid was evaluated by equation (E-2), and the degree of extraction(% extraction efficiency) was calculated by equation (E-3).

$$M_{Acid} \times V_{Acid} = M_{NaOH} \times V_{NaOH} \quad \text{(E-1)}$$

$$K_D = [HA]org / [HA]aqs \quad \text{(E-2)}$$

$$\% E = K_D / (1+ K_D) \times 100 \quad \text{(E-3)}$$

III. RESULSTS AND DISCUSSION

A. Effect of Contact Time

It is very important to study the contact time between an aqueous phase and organic phase for the proper mixing of phases. According to the literature review the contact time or shaking time is varied from 3 to 12 hours therefore it is necessary to optimize the contact time for shaking as per energy intensive aspect. Table 1 shows the results:

TABLE 1
Optimization of time at 303 K for the caproic acid concentration of 0.03 mol/l using mixed extractant

Time (hour)	Final acid conc. $[HA]_{aqs}$ (mol/l)	Final acid conc. $[HA]_{org}$ (mol/l)	Efficiency %E
1	0.00230	0.02770	92.33
2	0.00159	0.02841	94.70
3	0.00149	0.02851	95.03
4	0.00138	0.02862	95.40
5	0.00132	0.02868	95.60

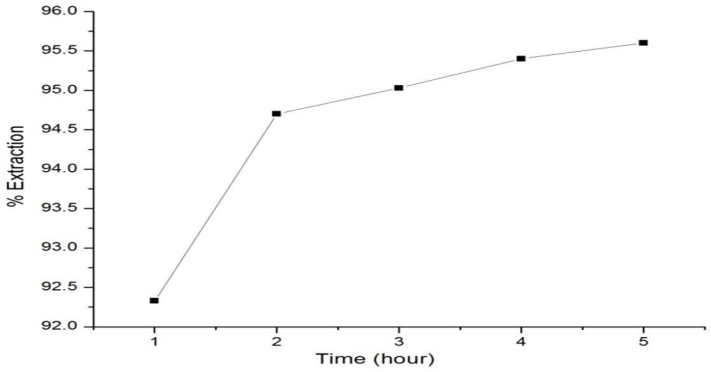


Fig 1 Variation of % Extraction with Time for acid concentration of 0.03 mol/l at 303 K

©IJRASET: All Rights are Reserved

An experiment is performed to optimize the contact time for the acid concentration of 0.03 mol/l and time is varied from 1 to 5 hours. Fig 1 shows the variation of % Extraction with time, from above graph it can be said that extraction efficiency is continuously increasing with time between time intervals 1 to 3 hours after that very less change is observed in extraction efficiency. So that optimum time for the shaking can be taken as 3 hours.

B. Physical Extraction of Caproic Acid

Physical extraction is performed without adding the extractant into the organic phase. Two non-toxic diluents (jatropha oil and soybean oil) are taken into consideration for the physical extraction of caproic acid. All the obtained results K_D and % extraction are tabulated in table 2.

Table 2
Distribution coefficient and degree of extraction for jatropha oil and soybean oil for Physical Extraction

S. No.	$[HA]_o$ (mol/l)	K_D	% E	K_D	% E
		Jatropha oil		Soybean oil	
1	0.01	0.56	35.92	0.59	36.99
2	0.02	1.63	61.99	1.74	63.50
3	0.03	2.44	70.90	2.53	71.67
4	0.04	3.20	76.19	3.30	76.75
5	0.05	3.79	79.12	3.90	79.60
6	0.057	4.26	80.98	4.33	81.23

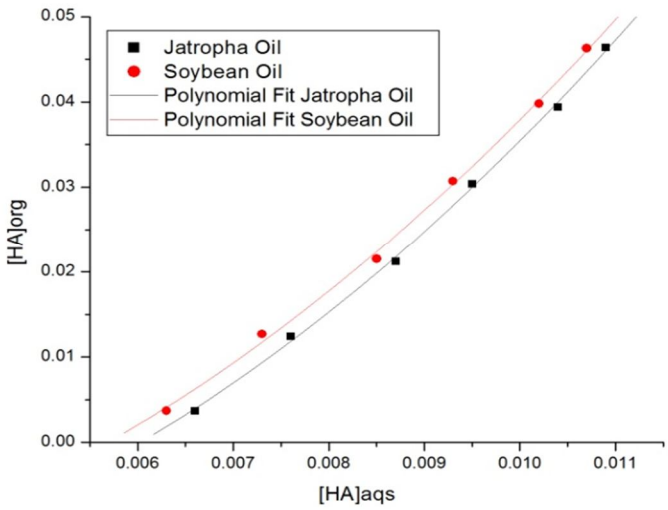


Fig 2 Physical Extraction equilibria data for Caproic acid in jatropha oil and soybean oil

Fig 2 shows the graphical representation of the variation of final acid concentration in organic phase with the final acid concentration in aqueous phase. K_D values and extraction efficiency are found to be increasing with initial acid concentration for jatropha oil and soybean oil as well. An equilibrium curve is plotted and found to be polynomial fitted.

C. Effect of Mixed Extractant

Mixed extractant play a major role in order to enhance the distribution coefficient and percentage extraction efficiency as compared to physical extraction. The possible values of distribution coefficient and degree of extraction are tabulated in table 3. Large significant change is observed in both the values i.e. distribution coefficient (K_D) and degree of extraction (% E) as compared to that of physical extraction with jatropha oil and soybean oil respectively.

©IJRASET: All Rights are Reserved

Table 3
Distribution coefficient and degree of extraction for jatropha oil and soybean oil for Reactive Extraction

S. No.	$[HA]_o$ (mol/l)	K_D	% E	K_D	% E
		Jatropha oil		Soybean oil	
1	0.01	6.63	86.90	6.56	86.80
2	0.02	13.08	92.90	13.39	93.05
3	0.03	18.87	94.97	19.13	95.03
4	0.04	24.16	96.03	24.97	96.15
5	0.05	29.12	96.68	30.06	96.78
6	0.057	31.76	96.95	33.54	97.11

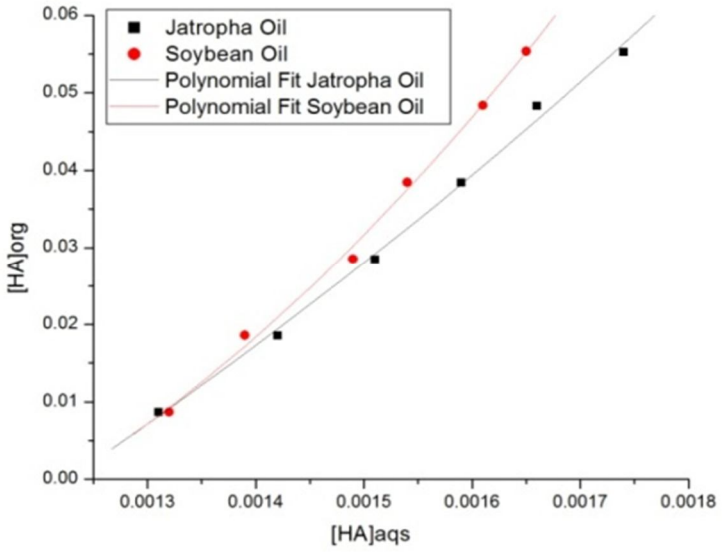


Fig 3 Reactive Extraction equilibria data for Caproic acid in jatropha oil and soybean oil

Fig 3 shows the graphical representation of the variation of the final concentration of acid in organic phase with final concentration of acid in aqueous phase. All the calculated values and depicted equilibrium curve is found to be best polynomial fitted with second order.

IV. COCNCLUSION

Reactive extraction is one of an alternative separation method over the other methods available for the extraction of various valuable carboxylic acids due to its convenience, less energy consumption and less waste generation and the problem of toxicity may be reduced in this technique. In this research study, the following conclusion can be drawn:

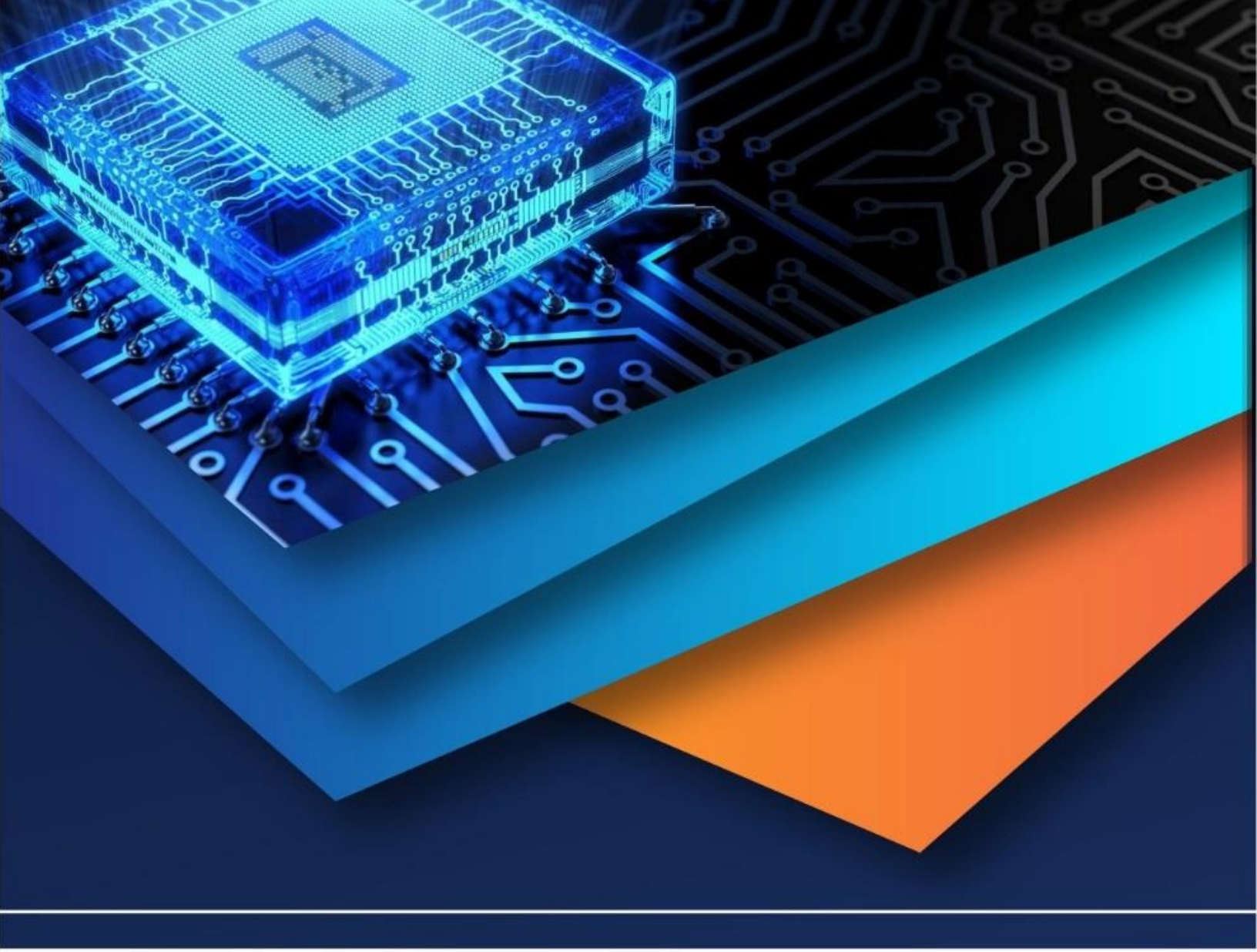
A. The optimum time for the shaking given to the incubator orbital shaker is observed as 3 hours.
B. The values of distribution coefficient for the physical extraction are obtained in the range of 0.56 to 4.26, 0.59 to 4.33 for jatropha oil and soybean oil respectively.
C. The values of degree of extraction for the physical extraction are obtained in the range of 35.92 to 80.98, 36.99 to 81.23 for jatropha oil and soybean oil respectively.
D. Similarly, the range of distribution coefficient for the chemical extraction is found as 6.63 to 31.76 and 6.56 to 33.54 for jatropha oil and soybean oil respectively.
E. Extraction efficiency is calculated in the range of 86.90 to 96.95 for jatropha oil and 86.80 to 97.11 for soybean oil for the chemical extraction of caproic acid.
F. Soybean oil is found to be the better diluent than the jatropha oil for the physical extraction and chemical extraction of caproic acid.

©IJRASET: All Rights are Reserved

REFERENCES

[1] Harington, T., Hossain, Md. M, Extraction of Lactic Acid into Sunflower Oil and Its Recovery into an Aqueous Solution, Desalination, 218(2008) 287-296.
[2] Keshav, A., Wasewar, K. L., Chand, S, Reactive Extraction of Propionic Acid using Tri-n-Octylamine, Tri-n-butyl Phosphate and Aliquat 336 in Sunflower Oil as Diluent, Journal of Chemical Technology and Biotechnology, 84 (2009) 484-489.
[3] Keshav, A., Norge, P., Wasewar, K. L,Reactive Extraction of Citric Acid Using Tri-n-octylaminein Nontoxic Natural Diluents: Part 1—Equilibrium Studies from Aqueous Solutions, Applied Biochemistry and Biotechnology, 167 (2012)197–213.
[4] Uslu, H., Gemici, A., Gök, A., Kırbaşlar, İ, Reactive Extraction of (E)-butenedioic Acid (fumaric acid) by Nontoxic Diluents, Journal of Chemical and Engineering Data, 59 (2014) 3767−3772.
[5] Waghmare, M. D., Wasewar, K. L., Sonawane, S. S., Shende, D. Z., Natural Nontoxic Solvents for Recovery of Picolinic Acid by Reactive Extraction, Industrial and Engineering Chemistry Research, 50 (2011) 13526–13537.
[6] Levy, P. F.; Sanderson, J. E.; Ashare, E.; Riel, S. R. de. Alkane Liquid Fuels Production from Biomass In: Wise D. L., ed, CRC Liquid Fuels Developments, CRC Boca Raton, Fla, 1983 pp 159-188
[7] Levy, P. F.; Sanderson, J. E.; Ashare, E.; Wise, D. L., Biorefining of Biomass to Liquid Fuels and Organic Chemicals, Enzyme Microb. Technol., 3(1981) 207-215.
[8] Levy, P. F.; Sanderson, J. E.; Ashare, E.; Wise, D. L.; Molyneaux, M. S. Liquid Fuels Production from Biomass. United States Dept of Energy Report, DOE/ET/20050-T4, US Department of Energy, Washington, DC. 1980.
[9] Kailas L. Wasewar and Diwakar Z. Shende. Extraction of Caproic Acid Using Tri-n-butyl Phosphate in Benzene and Toluene at 301 K. J. Chem. Eng. Data 55, (2010) pp. 4121–4125.
[10] Kailas L. Wasewar and Diwakar Z. Shende. Reactive Extraction of Caproic Acid Using Tri-n-butyl Phosphate in Hexanol,Octanol, and Decanol. J. Chem. Eng. Data , 56, (2011) pp. 288–297.
[11] Kailas L. Wasewar and Diwakar Z. Shende. Equilibrium for the Reactive Extraction of Caproic Acid Using Tri-n-butyl Phosphate in Methyl Isobutyl Ketone and Xylene. J. Chem. Eng. Data , 56, (2011) pp.3318–3322.
[12] Kailas L. Wasewar and Diwakar Z. Shende.Equilibrium Study for Reactive Extraction of Caproic Acid in Mibk and Xylene. Engineering,3, (2011) pp.829-835 .
[13] Kailas L. Wasewar et al. Reactive Extraction of Caproic Acid using Tri-n- Butyl Phosphate in Non Toxic Diluents. International Journal of ChemTech Research,11, (2018) pp. 56-62.

©IJRASET: All Rights are Reserved



10.22214/IJRASET

45.98

IMPACT FACTOR: 7.129

IMPACT FACTOR: 7.429

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Call : 08813907089 (24*7 Support on Whatsapp)