

Process Intensification Using Phase Transfer Catalysts

¹Sudarshan jadav, ²Dr.P.Shashikala, ³AR Ahmed razvi

University college of technology, Osmania university, Hyderabad, Telangana, India.

Abstract: Phase Transfer Catalyzed Alkylation of Sodium Benzoate and Butyl Bromide has been investigated in the present study. The work is aimed to determine the conversion of Butyl Benzoate, an important anti-bacterial food additive and food preservative, using various Quaternary Ammonium and Phosphonium Salts as catalysts. The reaction was studied using toluene as solvent at different temperatures, agitation speeds, varying moles of catalysts and at different molar ratios of reactants to determine the best possible parameters for obtaining good conversion of the product. It was observed that a yield of 98% was obtained with Tetra Phenyl Phosphonium Bromide catalyst in toluene at a temperature of 60°C and reaction time of 60 minutes. The obtained product was analyzed using titrimetric method.

Keywords: Phase Transfer Catalyst, Process Intensification, Speed, Time, Temperature, Moles, %Conversion.

I. INTRODUCTION

Process intensification is defined as any chemical engineering development that leads to a substantially smaller, cleaner and more energy-efficient technology¹. Process intensification aims at increasing the productivity as defined by the relationship between production of an output and all the resource inputs used in accomplishing the assigned task². Many approaches can be adopted for process intensification in the chemical and process industry.

A variety of liquid-liquid and liquid-solid reactions have been intensified and made selective by using simple phase-transfer (PT) catalysts such as quats, polyethylene glycol-400, etc., which allow ionic species to be ferried from aqueous phase to organic phase. Thus, the problems associated with extremely low solubility of the organic reactants in the aqueous phase can be overcome. In the pesticide and pharmaceutical industries, PTC is used extensively and has changed the fundamentals of business.

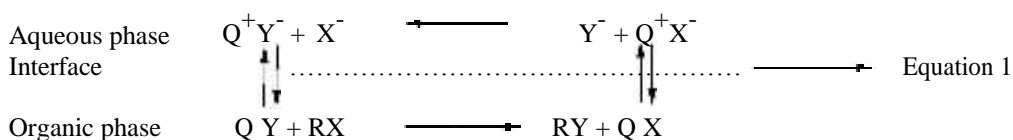
The development of novel equipment or methods is the key activities for process intensification. Aqueous-organic reactions are characterized by extremely low solubility of the organic reactants in the aqueous phase. This problem can be overcome by incorporating a phase transfer catalyst (PTC). A PTC is added to the system to transfer a functional reactant ion or group from one phase to another phase where it can rapidly react with another reactant³.

Based on the assumption that a reaction between lipophilic and hydrophilic reaction is facilitated by enhancement of mutual solubility, the transfer of a solute between phases is crucial for the establishment of liquid-liquid distribution equilibria⁴. Thus, high mass-transfer rate is required, which can be achieved by increasing the area of the interface⁵. Phase-Transfer Catalysis (PTC) is a well-known method of promoting reactions between reagents with opposite solubility preferences. In such systems each reactant is dissolved in the appropriate solvent. Commonly, the two solvents are immiscible to one another and then a phase transfer catalyst is added to facilitate the transport of one reactant into the other phase.

In the seventies, PTC became a method for overcoming problems of mutual solubility with Simultaneous activation of anions⁶ and was originally employed for reactions between ionic compounds and organic, water insoluble substances in solvents of low polarity⁷. Later, PTC included extraction of cations or even neutral molecules from one phase into another by means of the catalyst. Inverse phase transfer catalyzed extraction of species into the water phase was also studied

using partially water-soluble pyridines^{8,9}.

The mechanism of PTC reaction was first proposed in 1971¹⁰ According to Starks' original work, a quaternary ammonium halide dissolved in the aqueous phase (Q^+X^-) undergoes anion exchange with the anion of the reactant dissolved in the aqueous solution. The ion-pair formed (Q^+Y^-) can cross the liquid-liquid interface due to its lipophilic nature and diffuses from the interface into the organic phase, this step being the phase transfer in the organic phase, the anion of the ion-pair being quite nucleophilic undergoes a nucleophilic substitution reaction with the organic reagent forming the desired product (RY). The catalyst subsequently returns to the aqueous phase and the cycle continues. An overview of PTC reactions is given in the scheme below:



A prerequisite for a substance to function as a PT-Catalyst is to form ion-pairs soluble in the organic phase and to be transferred in a highly active state^{11,12}.

II. MATERIALS AND METHODS

MATERIALS:

Chemicals Used:

1. Sodium Benzoate
2. Butyl bromide
3. Toluene
4. Phenolphthalein indicator
5. Sodium Hydroxide

Catalysts Used:

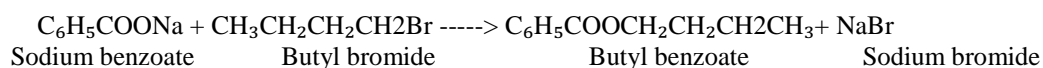
1. Tetra phenyl Phosphonium Bromide (TPPB)
2. Tri Capryryl methyl Ammonium Chloride (Aliquat 336)
3. Tetra butyl Ammonium Bromide (TBAB)

DETAILS OF THE TOOLS USED: Heating Mantle, Digital Stirrers (Remi), Water bath-thermostatic, Stop clock and Thermometer.

GLASSWARE USED: Three-necked round bottomed flask, Condenser, Beakers, Glass stirrer, Measuring jar, Conical flask, Separating funnel, Pipette and Burette.

III. EXPERIMENT

OVERALL REACTION:



Methodology:

The experiment was carried in a 500 ml three necked round bottomed flask. One of the two side necks was equipped with a condenser and the other with a thermowell. A thermometer placed in the thermowell containing glycerol is used for temperature measurement inside the reactor. A two-blade glass stirrer connected to remi stirrer was arranged inside the reactor. A regulator is used to control the speed of the stirrer; Digital Tachometer of remi stirrer apparatus reflects the speed. Round bottomed flask is placed in heating mantle; the temperature is controlled by using regulator.

Procedure:

The three necked 500ml round-bottomed flask, equipped with a mechanical stirrer, a thermometer. sodium benzoate and Butyl Bromide of 1:1 mole ratio (0.02 moles each) mixed in 100 ml of toluene and 100ml water as solvents.0.001 moles

of phase transfer catalyst is being added. Then, the contents of the flask were heated up to 60°C. The reaction mixture was stirred for about 1 hour. Samples were taken every 15 minutes from organic layer with fractional pipette (1 ml to 5 ml) into an analytical flask and product conversion was determined by saponification reaction.

Phase transfer alkylation of Sodium Benzoate with Butyl Bromide is performed in the presence of Toluene using tetra phenyl phosphonium bromide, tetra butyl Ammonium bromide, tri capryryl methyl ammonium chloride (Aliquat 336). The course of the reaction is followed with titrimetric analysis. Organic product is isolated and the conversion of the product Butyl Benzoate is estimated.

Analysis of the product:

The product formed in the phase transfer catalysis reaction is butyl benzoate. It is soluble in organic solvents but insoluble in water. When butyl benzoate is shaken with water, two liquid layers will be formed. The upper layer is butyl benzoate (less dense) and the lower layer is water. The samples drawn from the organic layer of PTC reaction were taken into a 25ml small conical flask. The flask is kept in boiling water for about 15 minutes for heating the contents. Phenolphthalein indicator is added to the flask. Then 0.0002M solution of NaOH is added. The reaction takes place in conical flask yielding sodium benzoate. After the reaction reaches to completion, any further NaOH addition causes the solution in flask to be basic and is indicated with pink color due to the presence of phenolphthalein indicator. The concentration of reactant is then calculated from the amount of base consumed in the reaction. Conversion of the product is then determined.

SAMPLE CALCULATION:

Concentration of NaOH solution (M_2) = 0.0002M

Concentration of Butyl Benzoate (M_1) = ?

Volume of Butyl Benzoate to be titrated (V_1) = 5 ml

Volume of NaOH consumed in titration (V_2) = 4 ml

From the formula: $M_1V_1 = M_2V_2$

$$M_1 = M_2V_2/V_1$$

$$M_1 = 0.00016M$$

The number of moles of product is given as:

$$0.00016 \times 100 \text{ ml} = 0.016 \text{ moles}$$

The amount of product can thus be given as:

$$(0.016 / 0.02) \times 100 = 80\% \text{ of reactant converted to product.}$$

IV. RESULTS AND DISCUSSIONS

EFFECT OF SPEED ON CONVERSION USING DIFFERENT CATALYSTS:

Reactions were carried out at a constant temperature of 60°C with 1:1 molar ratio of Sodium Benzoate(2.88gms) to Butyl Bromide(2.1ml), 0.001 mole of Tetra Phenyl Phosphonium Bromide(TPPB), Tri Capryryl methyl Ammonium Chloride (Aliquat 336), Tetra Butyl Ammonium Bromide (TBAB) as catalysts with 100 ml of toluene and 100ml of water as solvents. The speed of agitation was varied from 0 rpm to 700 rpm.

TABLE 1

S.NO	SPEED (RPM)	%CONVERSION USING TPPB	%CONVERSION USING ALIQUAT 336	%CONVERSION USING TBAB
1	0	40	38	40
2	300	86	78	77
3	400	94	89	87
4	500	96	92	91
5	600	96	92	91.6
6	700	96.2	92.4	91.6

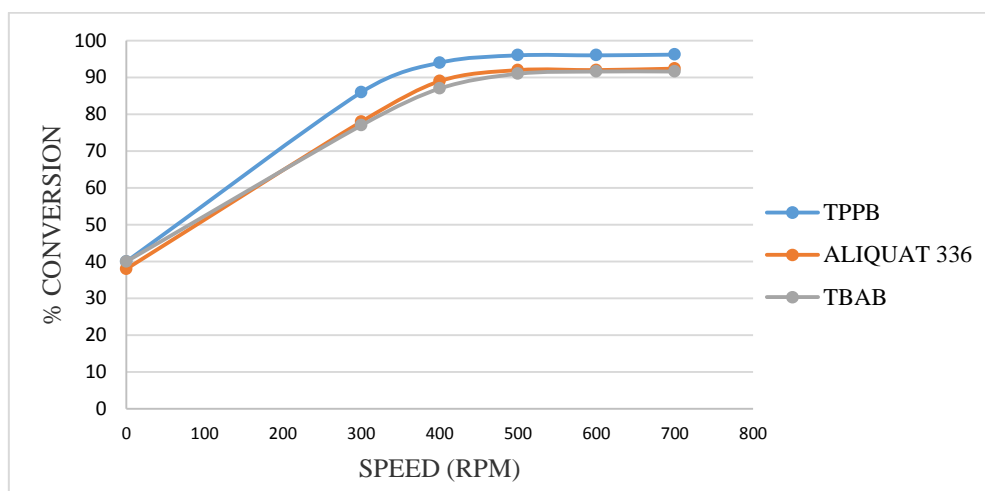


Fig. 1. Effect of stirrer speed

DISCUSSION: It is clear from the graph that conversions are obtained under non stirring conditions. This conversion is because of the reaction at the interphase. Upon stirring the conversion increases due to the increase in the mass transfer coefficient and a maximum conversion of 96% with respect to sodium benzoate is obtained at a stirrer speed of 500 rpm and even with further increase in stirrer speed the conversion remains almost constant for any further increase in the speed, which depicts that after 500 rpm reaction is independent of mass transfer coefficient. Hence subsequent experiments are carried out at a constant speed of 500 rpm. It is clear from the graph that a 96% conversion is the maximum conversion obtained using TPPB catalyst followed by ALIQUAT 336 and TBAB to be 92% and 91% respectively.

EFFECT OF REACTION TIME ON CONVERSION USING DIFFERENT CATALYSTS:

Reactions were carried out with a temperature of 60°C with 1:1 molar ratio of sodium benzoate to Butyl bromide, 0.001 mole of above catalysts. The speed of agitation was maintained 500 rpm as inferred from first experiment and reaction maintained for 90 minutes.

TABLE 2

S.NO	TIME (min)	%CONVERSION USING TPPB	%CONVERSION USING ALIQUAT 336	%CONVERSION USING TBAB
1	0	0	0	0
2	15	56	55	48
3	30	84	77	70
4	45	92	86	82
5	60	96	92	91
6	75	96.2	92.4	91.6
7	90	96.2	92.4	91.6

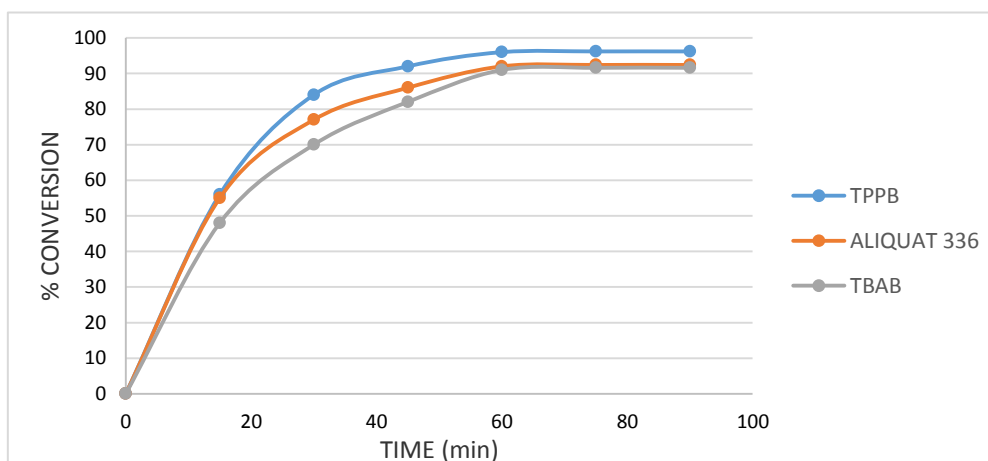


Fig. 2. Effect of varying time

DISCUSSION: Conversion increases with time. It is clear that the maximum conversion of sodium benzoate is obtained after 60 minutes is the maximum of 96% obtained with TPPB catalyst and remains almost constant for any further increase in time. Hence subsequent experiments with TPPB are carried out at a constant time of 60 minutes.

EFFECT OF TEMPERATURE ON CONVERSION USING DIFFERENT CATALYSTS:

Reactions were carried out at a constant speed of 500 rpm for 60 minutes with 1:1 molar ratio of Sodium Benzoate to Butyl Bromide, 0.001 moles of above catalysts with 100 ml of Toluene and 100ml of water as solvents. The temperature was varied from 30°C to 70°C.

TABLE 3

S.NO	TEMPERATURE (°C)	%CONVERSION USING TPPB	%CONVERSION USING ALIQUAT 336	%CONVERSION USING TBAB
1	30	34	32	30
2	40	64	60	58
3	50	80	78	77
4	60	96	92	91
5	70	96.4	92.4	91.6

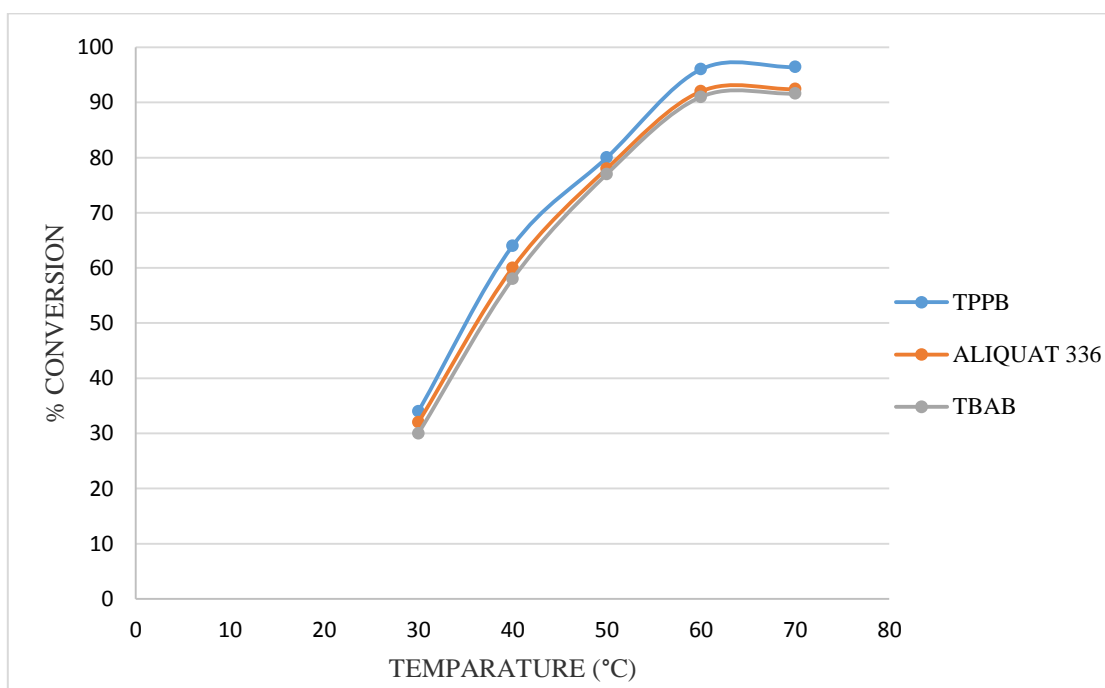


Fig. 3. Effect of varying temperature

DISCUSSION: Conversion increases with increase in temperature. With an increase in temperature from 30°C to 70°C, it has been observed that the conversion increases with increase in temperature to a maximum of 96% with TPPB catalyst. and further increase in temperature the conversion remains unchanged. Reaction suggests that butylation is an endothermic reaction.

EFFECT OF VARYING MOLES OF CATALYSTS ON CONVERSION:

Reactions were carried out at a constant speed of 500 rpm for 60 minutes with 1:1 molar ratio of Sodium Benzoate to Butyl Bromide and varying moles of catalysts with 100 ml of Toluene and 100ml of water as solvents. The reaction temperature of 60°C was maintained.

TABLE 4

S.NO	MOLES	Qty.in gms	% CONVERSION w.r.t TPPB	% CONVERSION w.r.t ALIQUAT 336	% CONVERSION w.r.t TBAB
1	0	0	0	0	0
2	0.0005	0.209	80	70	60
3	0.001	0.419	96	90	90
4	0.0015	0.628	98	94	93
5	0.002	0.838	98	94	93
6	0.003	1.25	98.2	94.5	93.5

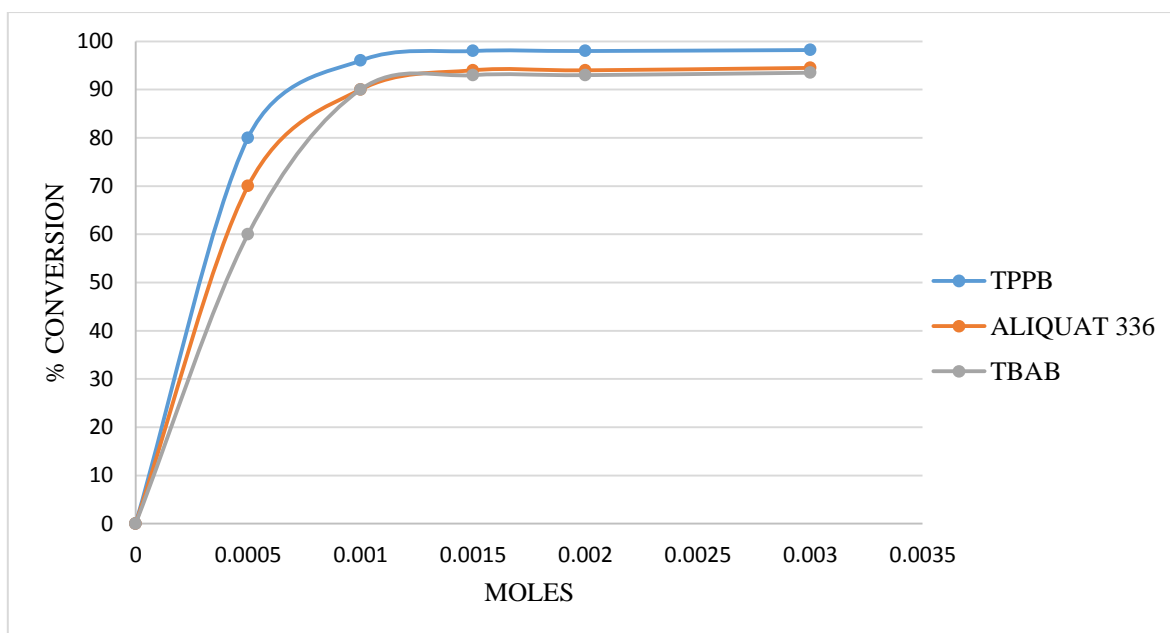


Fig. 4. Effect of varying moles of catalysts

DISCUSSION: It is clear that the maximum conversion of sodium benzoate is 98% which is obtained at a temperature of 60°C. With an increase in moles of catalysts from 0 to 0.0015 moles, it has been observed that the conversion increases sharply. It can thus be deduced that the 0.0015 moles of TPPB catalyst will be the optimal molar quantity for butyl benzoate production.

EFFECT OF VARYING MOLES OF REACTANT ON CONVERSION USING DIFFERENT CATALYSTS:

Reactions were carried out at a constant speed of 500 rpm for 60 minutes with 0.02 moles of sodium benzoate with varying moles of Butyl Bromide using 0.0015 molar quantities of different catalysts with 100 ml of Toluene and 100ml of water as solvents. The reaction temperature was fixed to 60°C.

TABLE 5

S.NO	MOLE OF BUTYL BROMIDE	Qty. in ml	% CONVERSION OF SODIUM BENZOATE USING TPPB CATALYST	% CONVERSION OF SODIUM BENZOATE USING ALIQUAT336 CATALYST	% CONVERSION OF SODIUM BENZOATE USING TPPB CATALYST
1	0.015	2.05	82	78	76
2	0.02	2.74	98	94	93
3	0.03	4.11	98	94	93
4	0.05	6.85	98	94	93
5	0.06	8.22	98	94	93
6	0.07	9.60	98	94	93

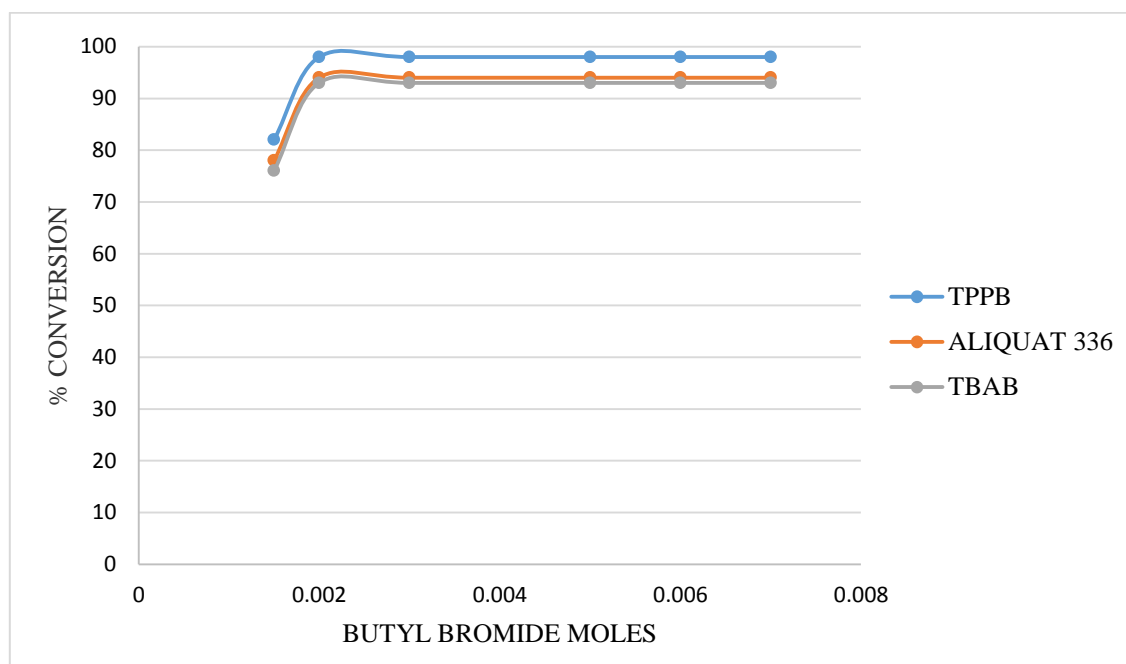


Fig. 5. Effect of varying moles of butyl bromide

DISCUSSION: It is clear that the maximum conversion of sodium benzoate is 98% which is obtained at a temperature of 60°C using TPPB catalyst. Thus it can be deduced that the following chemical reaction is an equimolar reaction for butyl benzoate production. i.e. The optimal conversion is possible at an equimolar reactant concentration.

V. CONCLUSIONS

1. Liquid-Liquid phase transfer reactions give increased conversions with quaternary ammonium and phosphonium salts.
2. Conversion increases with increase in stirring speed up to certain rpm and remains constant for any further increase of stirrer speed the conversions remain unchanged because beyond which the reaction is independent of mass transfer coefficient.
3. Conversion increases with respect to increase in temperature in all the cases. The reaction is endo-thermic. And at a maximum temperature 60°C about 98% conversions are achieved.
4. It can be concluded that Quaternary phosphonium salts give more conversion than Quaternary Ammonium salts.
5. The reaction of sodium benzoate with butyl bromide follows equimolar reaction.
6. The highest conversion of 98% is obtained at 500 rpm, 60°C and at a time period of 60 minutes with 0.0015 moles of tetra phenyl phosphonium bromide as catalyst.

REFERENCES

- [1] A.I. Stankiewicz, and J.A Mouljn, "Process Intensification: Transforming Chemical Engineering," Chem. Eng. Prog., vol. 96, pp. 22-34, Jan. 2000
- [2] S. Becht, R. Franke, A. Geibelmann, and H. Hahn, "An industrial view of process intensification," Chem. Eng. and Processing, vol.48, pp. 329-332, 2009
- [3] M.M. Sharma, "Strategies of conducting reactions on a small scale. Selectivity Engineering and process Intensification," Pure Appl. Chem., vol. 74, no. 12, pp. 2265-2269, 2002
- [4] K. F. Mattil, F. A. Norris, D. Swern, Extraction of fats and oils. In: Swern, D. (Ed.), *Bailey.s Industrial Oil and FatProducts*, third ed. John Wiley & Sons, London, (1964) 637.
- [5] L. A. Johnson, and E. W. Lusas, Comparison of alternative solvents for oil extraction. *J.Am. Oil Chem. Soc.* 60(2): (1983) 229.

- [6] H. K. Kim, Aqueous extraction of oil from palm kernel. *J. Food Sci.* 54, (1989) 491
- [7] C. Dennison and R. Lovrein, Three phase partitioning: concentration and purification of proteins. *Protein Expr. Purif.* 11, (1997) 149.
- [8] A. Sharma, M. N. Gupta, Three phase partitioning as a large scale separation method for purification of wheat germ bifunctional protease/amylase inhibitor. *Process Biochem.* 37, (2001)193
- [9] K. C. Rhee, C. M. Cater, and K. F. Mattil, Simultaneous recovery of protein and oil from raw peanuts in an aqueous system. *J. Food Sci.* 1972, 37, (1972) 90.
- [10] C. M. Starks, *J. Am. Soc.* 93, p 195 (1971)
- [11] C. De Ruiter, R. Otten, U. Brinkman, R. Frei, *J. Chromatogr.*, 436 (1988) 429.
- [12] H. J. Glatzer, L. K. Doraiswamy, *Chem. Engin. Sci.*, 55 (2000) 5149.