

Optimization of Reaction Parameters for Production of *p*-*tert*-butylbenzoic acid

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Abstract—Para-tertiary-butylbenzoic acid is produced by oxidizing *p*-*tert*-butyltoluene with air. *p*-*tert*-butylbenzoic acid is a colourless crystal and an important organic intermediate. It is mainly used for the preparation of fine chemicals, cosmetics, resin additives, nucleating agent, anticorrosive additive, polyethylene stabilization additive. In the present work, *p*-*tert*-butylbenzoic acid is produced by oxidizing *p*-*tert*-butyltoluene with air and with acetic acid as solvent, cobalt acetate as catalyst and sodium bromide as catalyst initiator in an autoclave. Thermochemistry calculations reveal that the oxidation reaction of *p*-*tert*-butyltoluene is feasible and is exothermic in nature. Equilibrium constant of the reaction indicate that the reaction is irreversible. The optimization of the reaction parameters such as reaction time, temperature, catalyst loading, and solvent quantity has been carried out in an autoclave and the reaction mixture analyzed using gas chromatograph. The results indicated the conversion is increased with increase in weight ratio of reactant to solvent, catalyst concentration and temperature. The reaction kinetics showed that the reaction follows pseudo first order reaction. The activation energy for the reaction is 24463.94 J/mol. The optimum conditions for the oxidation reaction are 130°C, 1:3 weight ratio and 5% of catalyst with respect to reactant weight.

Key Words: *p*-*tert*-butyltoluene, *p*-*tert*-butylbenzoic acid, acetic Acid, Sodium Bromide, Cobalt acetate, autoclave, gas chromatography.

1 INTRODUCTION

p-*tert*-butylbenzoic acid is a substituted benzoic acid. It is used as a process regulator in polymer industry for producing alkyd and polyester resin. *p*-*tert*-butylbenzoic acid could improve the colour and life service of alkyd resins as well as shortens the drying time. It is also used for the production of anti oxidant in metal cutting emulsion, rust inhibitors in resin coatings and lubricating oil and as a stabilizer. *p*-*tert*-butylbenzoic acid is mainly produced by oxidizing para-*tert*-butyltoluene with air or any gas containing oxygen as its composition. Nowadays, *p*-*tert*-butylbenzoic acid is widely used as a commercial product in developed countries. The commercial processes for oxidation of *p*-*tert*-butyltoluene to corresponding carboxylic acid is available in America, china, Japan etc. Several processes are reported for preparation of carboxylic acids by oxidation of toluene or toluene substituted on the nucleus. The oxidation systems include selective vapour phase oxidation under high temperature electrochemical oxidation and liquid phase catalytic oxidation under mild condition [1]. The conversion of vapour phase oxidation is 97%, whereas the yield of the product is about 62.4%. The yield of electrochemical oxidation is extremely poor (about 30%) and the process results in excessive electricity consumption [2]. The catalytic oxidation of *p*-*tert*-butyltoluene to *p*-*tert*-butylbenzoic acid under atmospheric pressure and high pressures were studied. The yield of *p*-*tert*-butylbenzoic acid at atmospheric pressure is 89% and under high pressure 95% yield is obtained [1]. In the present work the process for ox-

idation of *p*-*tert*-butyltoluene to *p*-*tert*-butylbenzoic acid is developed.

2. Material and Methods

2.2 Materials:

p-*tert*-butyltoluene, acetic acid, Cobalt acetate and Sodium bromide are supplied by SD Fine Chemicals, Hyderabad, India. Zero air cylinder is used for the supply of oxygen. Other reagents used in the present work are all of analytical grades and are used as received.

2.2 Methods:

2.2.1 Calculation of Gibbs free energy and heat of Reaction:

It is very important to know the thermochemistry of a reaction to evaluate the process before an actual experiment is performed. The Gibbs free energy and the enthalpy of reactions are calculated.

Gibbs free energy and heat of oxidation reaction are calculated from Joback group contribution method [3]. The calculations show that thermodynamically the reaction is feasible and it is exothermic reaction. The Gibbs free energy of the reaction is -511.01KJ/mol. This shows that the reaction is thermodynamically stable. The reaction is irreversible. The standard enthalpy of reaction shows that the reaction is exothermic in nature. The standard enthalpy of the reaction is -564.82KJ/mol.

2.2.2 Experimental Procedure:

The liquid phase catalytic oxidation of *p-tert*-butyltoluene to *p-tert*-butylbenzoic acid in acetic acid media is a typical aromatic hydrocarbon oxidation process. The oxidation of *p-tert*-butyltoluene experiments are carried in a Parr autoclave reactor. The autoclave is of 100ml capacity. The experiments for oxidation of *p-tert*-butyltoluene are carried in semi batch mode. The air is continuously fed to the reactor and all other reactants are charged into the reactor before start-up of the reaction.



Figure 1. Experimental Setup

The reaction temperature and pressure are maintained in the reactor as per conditions. In the oxidation of *p-tert*-butyltoluene, acetic acid is used as a solvent, cobalt acetate as catalyst and sodium bromide as a catalyst initiator. Different sets of experiments are carried out by varying the temperature, catalyst concentration and weight ratio of acetic acid to *p-tert*-butyltoluene. In reaction air pressure is maintained constant and temperatures are varied from 110°C to 130°C. The catalyst concentration is varied from 5-10% of PTBT. The weight ratio of *p-tert*-butyltoluene to acetic acid is varied from 1:2 to 1:5. After completion of the reaction the reaction mixture is discharged from the reactor and is cooled to room temperature. After cooling, the desired product will separate out as crystals that are washed with water and then dried at 80°C for 2hr.

2.3 Analysis:

Samples are collected at different time intervals during the course of the reaction. These samples are analysed by Gas Chromatography (GC-2010) using FID detector. The identification of reactant and product is through the known retention time of the pure authentic samples.

3. Results and Discussion

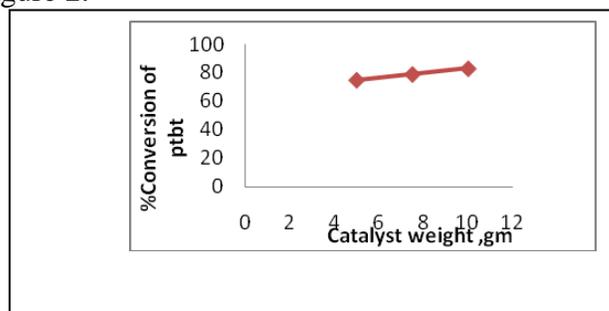
In gas-liquid reactions the reactant gas must enter the liquid phase for reaction to occur. The mass transfer resistance and the resistance of chemical reaction step need to be included in the overall rate reaction. The general rate expression for mass transfer with reaction is as follows [4].

$$-r'' = \frac{1}{\frac{1}{K_{Lg}a} + \frac{H_A}{K_{AL}aE} + \frac{H_A}{C_B k f_1}} P_A$$

Where the mass transfer coefficient and diffusivity of the reactants are necessary for calculation of the overall rate of the reaction. The diffusivities are calculated by using Wilke-chang equation. The mass transfer coefficients are calculated with the help of general dimensionless correlation.

3.1 Effect of catalyst on conversion of *P-tert*-butyltoluene

In the oxidation of *p-tert*-butyltoluene reaction the effect of catalyst concentration is studied keeping all other parameters constant and the results are presented in Figure 2.



From the Figure 2, it is evident that the conversion of *p-tert*-butyltoluene increases with increase in the catalyst concentration.

3.2 Effect of Temperature on conversion of *p-tert*-butyltoluene

In order to determine the effect of temperature on the conversion of *p-tert*-butyltoluene the reactions are carried out at 110, 120, 130 and 140°C temperatures.

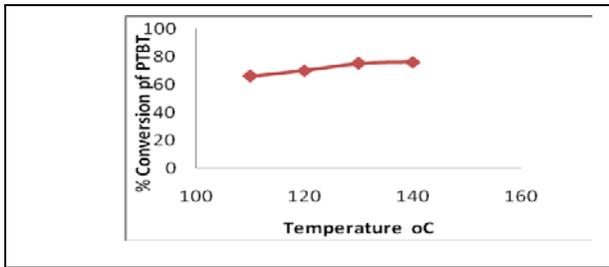


Figure 3: Effect of temperature on conversion of PTBT to PTBBA at 1:3 weight ratio at 5% catalyst and 10 bar pressure.

The results are presented in Figure 3, it is observed that as the temperature of the reaction is increased the conversion of *p-tert*-butyltoluene also increases. The experimental data at different temperatures show that a maximum conversion of 75% is obtained at 130°C.

3.3 Effect of weight ratio *p-tert*-butyltoluene to solvent on conversion of *p-tert*-butyltoluene:

In order to study the effect of weight ratio on the conversion of *p-tert*-butyltoluene, experiments are conducted at 1:2, 1:3 and 1:5 mole ratios of PTBT to acetic acid and the results are given in Figure 4.

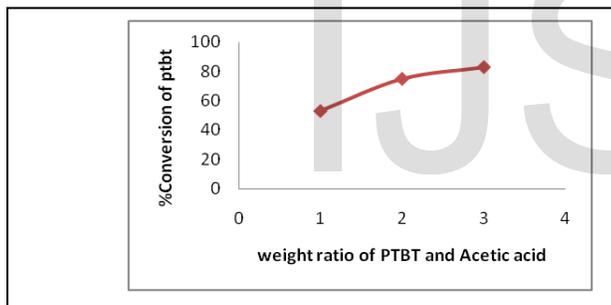
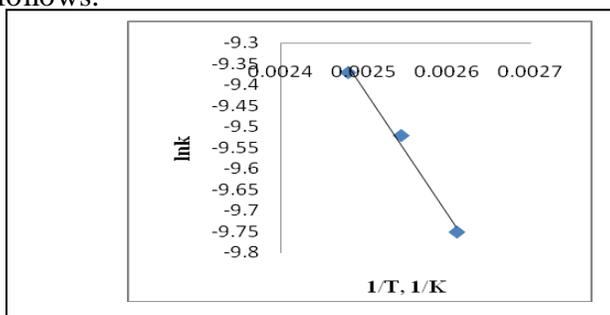


Figure 4: Effect of solvent quantity on PTBT conversion

From the experiments, it is observed that as increasing the weight ratio of *p-tert*-Butyltoluene to acetic acid the conversion of *p-tert*-butyltoluene increases.

3.4 Calculation of activation energy:

Arrhenius plot is drawn for calculation of activation energy of the reaction. The plot is of $\ln k$ v/s $1/T$ is as follows.



The activation energy of the reaction is 24491.88J mol⁻¹

4 CONCLUSION

In the present work *p-tert*-butylbenzoic acid is produced by oxidizing *p-tert*-butyltoluene with air and with acetic acid as solvent, cobalt acetate as catalyst and sodium bromide as catalyst initiator in an autoclave. The optimization of the parameters is studied. The maximum conversion of *p-tert*-butyltoluene is 75% and the weight ratio of *p-tert*-butyltoluene to acetic acid is 1:3. The present process is an economical process developed for producing *p-tert*-butylbenzoic acid and it is going to be commercialized

NOMENCLATURE

f_L	Liquid hold-up
α	Specific Interfacial area
V_L	Volume of liquid
S	Gas-liquid interfacial area
Φ	gas hold-up
ΔG_{F298}°	Gibbs free energy of formation at 298.15K, KJ/mol
ΔH_{F298}°	Enthalpy of formation at 298.15 K, KJ/mol
X_R	Conversion of reactant
$K_{A=}$	Gas phase mass transfer coefficient
K_{AL}	Liquid phase mass transfer coefficient
E	Liquid film enhancement factor
C_R	Concentration of reactant
H_A	Henrys constant
k	Rate constant
R	Real gas constant
A	Pre-exponential factor
T	Temperature
D_{AL}	Diffusivity
PTBT	<i>p-tert</i> -butyltoluene
PTBBA	<i>p-tert</i> -butylbenzoic acid

REFERENCES

1. <http://ru.p-toluenesulfonicacid-ptbba.com/News/10.22.htm>

2. Ahmed anwar amin, "catalytic oxidation of 4-t-butyltoluene" a thesis submitted for the degree of doctor of philosophy of the university of sydney october 2002.
3. Nada Mohammed Al-Ananze "Oxidation Processes: Experimental Study and Theoretical Investigations" Dissertation work for Degree of Doctor of Philosophy, April 2004.
4. R.M. Cole, A. W. Fairbairn and K. D. Detling "The development of a process for the manufacture of p-tertiary-butylbenzoic acid," Special Supplement to Chemical Engineering Science, Vol. 3, 1954.
5. J. Hakotier and M. hanoteer-bridoux "Mechanism of the liquid phase homogeneous oxidation of alkyl aromatic hydrocarbons by cobalt salts" Journal of Molecular Catalysis, 12, 133 – 147, 1981.
6. Wolfgang F. Hoelderich and Felix Kollmer "Oxidation reactions in the synthesis of fine and intermediate chemicals using environmentally benign oxidants and the right reactor system" ,Pure Appl. Chem., Vol. 72, No. 7, pp. 1273–1287, 2000.
7. Akkihebbal Krishnamurthy Suresh Man Mohan Sharma and Tamarapu Sridhar "Engineering Aspects of Industrial Liquid-Phase Air Oxidation of Hydrocarbons," Ind. Eng. Chem. Res, 39, 3958-3997, 2000.
8. J. Lozar, D. Bejan and A. Saval "Liquid-phase p-t-butyltoluene autoxidation enhanced by electrochemistry: Activation of the catalytic effect of cobalt acetate," Journal of Applied Electrochemistry 32 839–844, 2002.
9. Hanna kierzowska-pawlak, "Determination of kinetics in gas-liquid reactions systems. an overview", ecol chem eng s. 19(2):175-196, 2012.
10. Marcel Feld , Cologne " Process for the preparation of aromatic monocarboxylic acids from toluene and substituted toluenes" , United states patent patent number 4603220 Jul 29 1986.
11. Leon G. A. van de Water, Arati Kaza, James K. Beattie, Anthony F. Masters, and Thomas Maschmeyer "Partial Oxidation of 4-tert-Butyltoluene Catalyzed by Homogeneous Cobalt and Cerium Acetate Catalysts in the Br⁻/H₂O₂/Acetic Acid System: Insights into Selectivity and Mechanism", Chem. Eur. J. 13, 8037 – 8044, 2007.
12. A. s. vaze, S. b. sawant, V. g. Pangarkar "Electrochemical oxidation of p-t-butyltoluene to p-t-butylbenzaldehyde", Journal of applied electrochemistry 28 623-626, 1998.
13. Qinbo Wang ,Yongzhao Zhang, Youwei Cheng and Xi Li, "Reaction Mechanism and Kinetics for the Liquid-phase Catalytic Oxidation of meta-Xylene to meta-Phthalic Acid"
14. Tatiana V. Bukharkina and Nikolai G. Digurov "Kinetics of Aerobic Liquid-Phase Oxidation of Organic Compounds"

15. Periana et al “Oxidation of tertiary-alkyl substituted aromatics” United states patent , patent number 5068407 nov.26 1991.
16. Wanyi Li Yonghua Xu Jiaqiang Wang Zhongbiao Zhai Zhiying Yan Yalin Yang, “Selective Oxidation of 4-Tert-butyltoluene to 4-Tert-butylbenzaldehyde Over Co/MCM-41” , Catal Lett 119:327–331 DOI 10.1007/s10562-007-9239x ,2007.
17. L. Kucka, J. Richter, E.Y. Kenig , A. Go´rak “Determination of gas_ liquid reaction kinetics with a stirred cell reactor”, Separation and Purification Technology 31 163-175,2003.
18. T.S.S. Rao and Shubhra Awasthi “Oxidation of Alkylaromatics”, E-Journal of Chemistry Vol. 4, No.1, pp 1-13 January 2007.
19. Felix Garcia-Ochoa ,Emilio Gomez, “Theoretical prediction of Theoretical prediction of gas–liquid mass transfer coefficient, specific area and hold-up in sparged stirred tanks Chemical engineering Science 59 , 2489-2501 ,2004.
20. R. H. Perry, D. W. Green, Prediction and Correlation of Physical Properties, “Perry’s Chemical Engineers’ Handbook”, Mc. Graw Hill, New Delhi.