Improvements in the manufacture of benzoic acid obtained by catalytic oxidation of toluene

Melhorias na fabricação de ácido benzóico obtido por oxidação catalítica de tolueno

João Guilherme Rocha Poço
ORCID: https://orcid.org/0000-0001-6764-6947
Centro Universitário FEI, Brazil
E-mail: jgrpoco@fei.edu.br
Rodrigo Cella
ORCID: https://orcid.org/0000-0001-8612-7376
Centro Universitário FEI, Brazil
E-mail: r.cella@fei.edu.br
Silas Derenzo
ORCID: https://orcid.org/0000-0001-8803-6961
Instituto de Pesquisas Tecnológicas do Estado de São Paulo S/A, Brazil
E-mail: derenzo@ipt.br

Abstract

This study investigates improvements in benzoic acid production through the catalytic oxidation of toluene with cobalt octoate. The oxidation process, which occurs under controlled conditions with temperatures ranging from 130 °C to 165 °C, typically results in a conversion rate of 50% toluene with a selectivity of 80% over benzoic acid. However, various by-products such as benzyl alcohol, benzaldehyde, and benzyl benzoate are also formed, which reduces the overall yield. The work identifies methods to minimize these byproducts, particularly benzyl benzoate, which forms in the distillation column. One strategy investigated involved using additives to inhibit the esterification reaction that produces benzyl benzoate, aiming to improve the selectivity of the oxidation process. Experimental results show that maintaining reaction temperatures between 135 °C and 145 °C in combination with using sodium benzoate as an additive effectively reduces the formation of benzyl benzoate and increases the yield of benzoic acid. Furthermore, increasing the O_2/toluene ratio increases the oxidation efficiency.

Keywords: Toluene catalytic oxidation. Obtention of benzoic acid. Promoters for cobalt octoate catalyst.

Resumo

Este estudo investiga melhorias na produção de ácido benzóico através da oxidação catalítica de tolueno com octoato de cobalto. O processo de oxidação, que ocorre sob condições controladas com temperaturas variando de 130 °C a 165 °C, normalmente resulta em uma taxa de conversão de 50% de tolueno com uma seletividade de 80% em relação ao ácido benzóico. No entanto, vários subprodutos, como álcool benzílico, benzaldeído e benzoato de benzila, também são formados, o que reduz o rendimento geral. O trabalho identifica métodos para minimizar esses subprodutos, particularmente o benzoato de benzila, que se forma na coluna de destilação. Com o objetivo de melhorar a seletividade do processo de oxidação, uma estratégia que foi investigada envolve o uso de aditivos para inibir a reação de esterificação que produz benzoato de benzila. Os resultados

experimentais mostram que a manutenção de temperaturas de reação entre 135 °C e 145 °C em combinação com o uso de benzoato de sódio como aditivo reduz efetivamente a formação de benzoato de benzila e aumenta o rendimento do ácido benzóico. Além disso, o aumento da relação O_2/tolueno aumenta a eficiência da oxidação.

Palavras-chave: Oxidação catalítica de toluene. Obtenção de ácido benzóico. Promotores para octoato de cobalto.

Nomenclature

FDCA – furan dicarboxylic acid
PET – polyethylene-terephthalate
HMF - hydroxymethylfurfural

1. Introduction

Benzoic acid is an aromatic carboxylic acid naturally present in plant and animal tissues, which microorganisms can produce. Benzoic acid and a wide range of derivatives and related benzenic compounds, such as salts, alkyl esters, parabens, benzyl alcohol, benzaldehyde, and benzoyl peroxide, are commonly used as antibacterial and antifungal preservatives and as flavoring agents in food, cosmetic, hygiene, and pharmaceutical products. (Del_Olmo *et al.*, 2017)

Its production can be done either by biotechnological methods (Noda *et al.*, 2012; Zhou *et al.*, 2020) or catalytic oxidation of toluene in vapor and liquid phases. The liquid and vapor-phase oxidation of toluene by air or oxygen has been studied by many researchers using different catalysts to find conditions and catalysts for the selective oxidation to benzaldehyde or benzoic acid (Bulushev, 2004; Gast *et al.*, 2020; Gizli *et al.*, 2008; Hancock, 1992; Maki, 1998; Shengwei *et al.*, 2007).

In the present paper, toluene oxidation to benzoic acid was catalyzed by cobalt octoate as a representative of an industrial process. In that process, the batch homogeneous catalytic reaction occurs at 130 °C to 165 °C and takes 30 hours. From that, the toluene conversion is around 50%, with a selectivity of 80% (Maki, 1998).

Other chemical products are also produced as intermediates due to partial conversion or by-products during oxidation. Product purification is performed by fractional distillation, where the non-reacted toluene, benzaldehyde, and benzoic acid are recuperated. Toluene and benzaldehyde could be recycled in the process.

At the bottom of the distillation column flows a residue ("benzotar") rich in benzyl benzoate, a product formed by the reaction of benzylic alcohol and benzoic acid, which also occurs in the column. So, one way to improve the process's yield is to avoid this reaction inside the distillation column. Moreover, some biphenyls are formed, reducing the yield of the process.

This work aims to identify some alternatives to avoid the formation of intermediates and improve the yield of benzoic acid. One of the ways was to use some additives to enhance the toluene oxidation to benzoic acid.

2. Materials and Methods

The laboratory process set up to study the reaction is presented in Figure 1. It consists of a 1000 mL Parr-type reactor, mass flow and temperature controllers, reflux column, water separator decanter, and an analytical system with two chromatographs, one for analyzing the oxygen content (PM 5A) at the reactor outlet and another for analysis of the liquid reaction products (SE-30) (poco, 2003).

The reactor was charged with a mixture of toluene and cobalt octoate at 6% (Liosec HC) from Miracema-Nuodex at the desired concentration (70 g of Co/m3). The reactor pressure was then adjusted to that chosen by passing inert gas, and the reactor was heated to the desired temperature.

When the temperature was reached, the supply of synthetic air containing 9% or 21% O2 began, and the reaction time was counted. The airflow was adjusted to reproduce the O2/toluene

ratio used in the industrial process. At the same time, monitoring of the O2 content at the reactor outlet was started by gas chromatography using a 5A Molecular Sieve column (2 m x 1/8"). Every 30 minutes, a sample of the reaction liquid was collected from the reactor, and its composition was determined by liquid chromatography using a SE-30 column (3 m x 1/8"). The conditions of Chromatography analysis are presented in Table 1.

The tests continued until the O_2 content at the outlet exceeded the safety limit of 2% (v/v) to avoid entering the flammability limits.

The identification of byproducts and "benzotar" components was done using GC-MS.
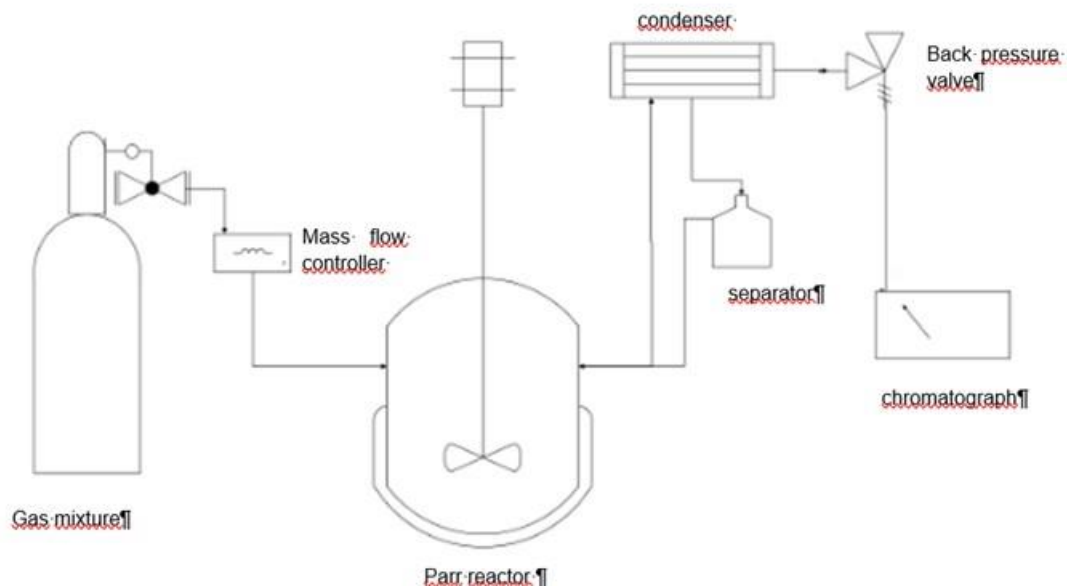

Figure 1 - Laboratory flow diagram of toluene oxidation

The tests continued until the O_2 content at the outlet exceeded the safety limit of 2% (v/v) to avoid entering the flammability limits.

The identification of byproducts and "benzotar" components was done using GC-MS.

Table 1 – Conditions of chromatography analysis.

	Effluent gas	**Liquid media**
Column	P. Molec. 5A	SE-30 (1.5%)
Length of column 1/8" (m)	2	3
Helium flow (mL/min)	30	30
Initial temperature (oC)	Tamb	70
1st program rate (oC/min)	-	7
Intermediate temperature (oC)	-	100
2ª program rate (oC/min)	-	13
Final temperature (oC)	Tamb	215
Total time (min)	3	17.1

3. Results and Discussion

The analysis results were compiled, and Figure 2 shows the evolution of the reagents toluene and some intermediates, products, and by-products of the reaction (ethylbenzene, benzaldehyde, benzyl alcohol, benzoic acid, benzyl benzoate, and dimethyl biphenyl) compared to the first hours of the reaction.

In this experiment, oxygen was present in the exit gas in the 0.2% to 0.65% range. Toluene concentration decreases linearly after the first two hours. In this same period, benzyl alcohol and benzaldehyde are formed, and after 1,5 hours, benzoic acid begins to form, and its concentration increases linearly. The toluene oxidation toward benzoic acid seems to occur according to the steps given in R1, R2, and R3. After the formation of benzoic acid, benzyl benzoate starts to form, indicating that it is formed by an esterification reaction between benzoic acid and benzylic alcohol (R4).
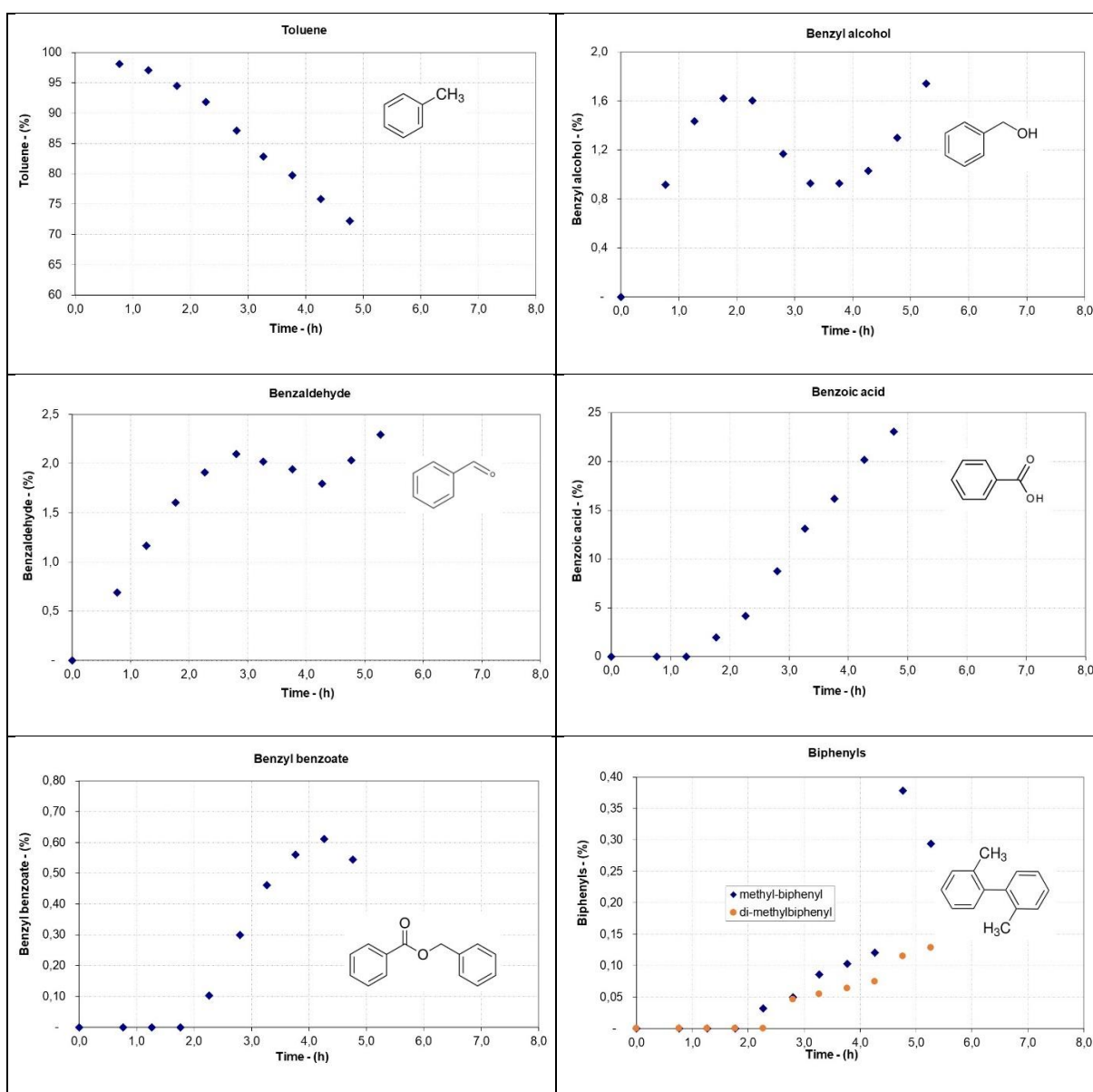

Figure 2 – Concentration (%m/m) evolution of raw materials and products of the reaction.

After some time, the content of benzyl benzoate decreased, probably due to hydrolysis caused by the increase of water content in reaction media, and so the benzyl alcohol increases and, consequently, the benzaldehyde.

The biphenyls are compounds with two aromatic rings, and they can be formed due to the reactions between intermediates or products and toluene. They were detected using GC-MS. The dimethyl-biphenyl and bi-benzyl (1,2 diphenyl-ethane) have the same molecular weight, despite the last could be formed by hydrodeoxygenative coupling of benzaldehyde (So *et al.*, 2023), as shown in Figure 2a e 2f, benzaldehyde begin to apper before one hour of reaction and the diphenylethane only after 2.5 hour of reaction. These bibenzyl or biphenyl compounds are found in the residue of the distillation column ("benzotar").

As cited before, a "benzotar" is a product from the bottom of the distillation column, where benzyl benzoate, an ester formed from benzoic acid and benzylic alcohol, is one of its principal components. So, reducing this formation results in a higher yield of benzoic acid in the process. Another way is to accelerate the oxidation of benzyl aldehyde and benzyl alcohol. The reduction of these substances is achieved by reducing the temperature since increasing the temperature increases the relation of benzylic alcohol + benzyl benzoate over benzoic acid formation (Figure 3).
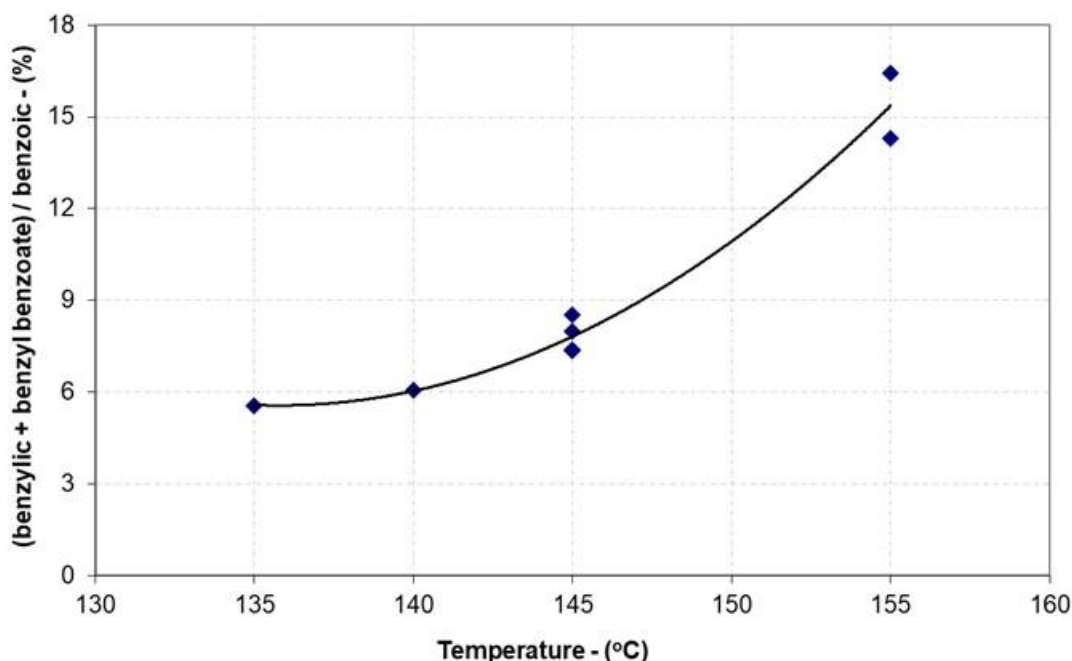

Figure 3 - Temperature effect in relative selectivity

Increasing 40% of O_2 in the feed increased the formation of oxidation products (benzaldehyde, benzyl alcohol, benzoic acid, benzyl benzoate, and others) from 19.4 % to 29.6 % and controlling the amount and form of addition of the catalyst.

Increasing water in reaction media could cause benzyl benzoate to hydrolyze according to the reversible reaction (R4). If it is true, then it is expected that more prolonged time reactions or conversions could increase selectivity (Figure 4, 5).

It was observed that the use of additives could improve selectivity. Fourteen additives were evaluated, most of them sodium salts, as promoters to inhibit benzyl benzoate formation, probably catalyzing its hydrolysis (R4).

Table 2 presents the verified effects of some substances indicated in the literature and others chosen for the possible effects that could induce the reaction. Among the substances indicated in the literature, such as sodium fluoride, sodium pyrophosphate, and bromide (Bonnart *et al.*, 1968; Partenheimer, 1998) that supposedly increase selectivity to benzaldehyde, none of them showed this effect. The Na+ ion, used here in the form of sodium benzoate, which would have the same effect of increasing selectivity to benzaldehyde (Takao *et al.*, 1984) in this study, had the effect of reducing

the formation of benzyl benzoate and benzyl alcohol, the latter, as already mentioned, consumes part of the benzoic acid in the distillation column, increasing the amount of benzyl benzoate and therefore "benzotar".

It was observed that the presence of acetic acid in the reaction practically inhibits the formation of benzyl benzoate. However, it increases the formation of benzyl acetate and acetophenone formation at levels almost equivalent to benzyl benzoate usually formed. Acetic acid could be advantageous, as the benzyl acetate formed has a lower boiling point than benzoic acid. Therefore, it could be recovered in the distillation column.
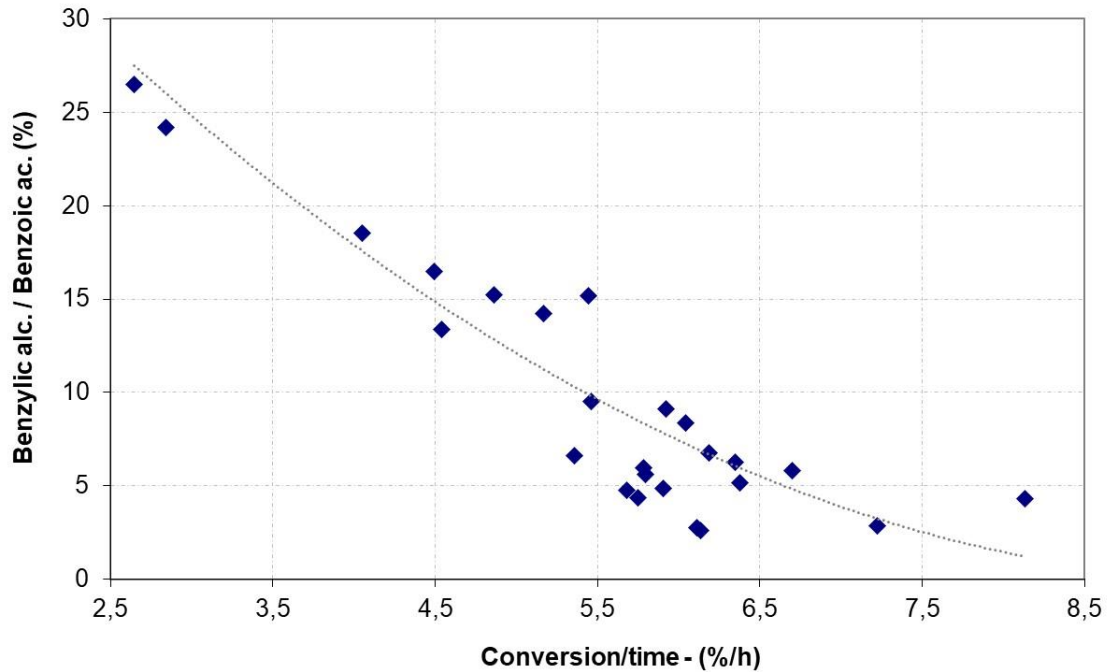

Figure 4 - Effect of rate of conversion over benzylic alc. / benzoic acid.
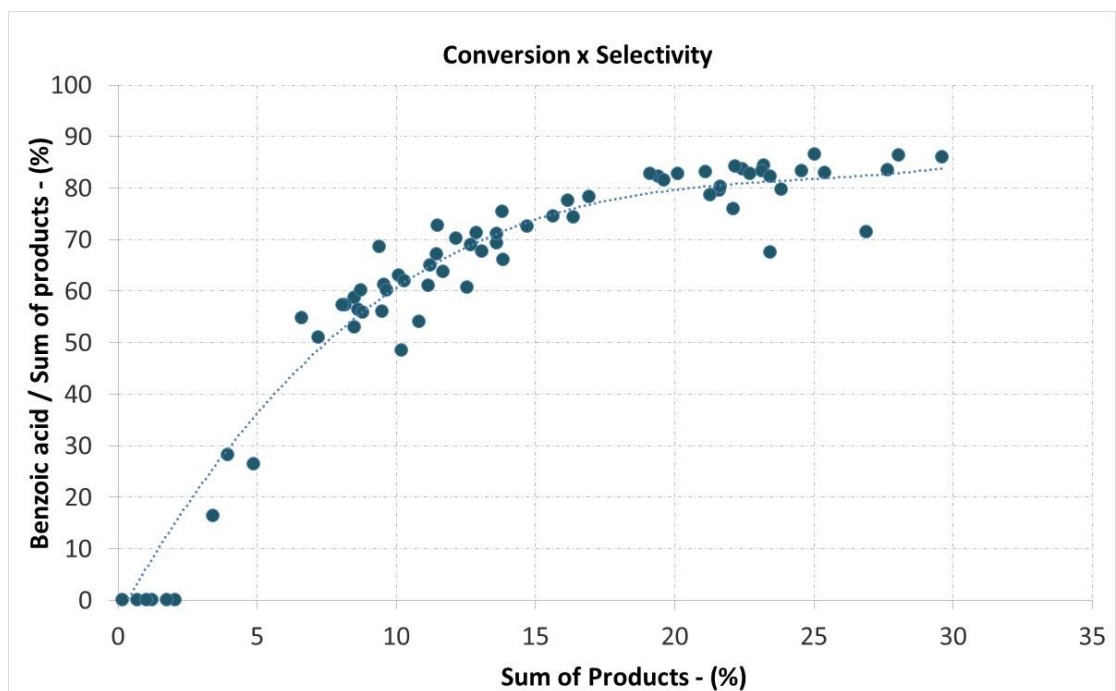

Figure 5 - Effect of conversion extension over total selectivity.

Table 3 contains some data on possible alternative catalysts to cobalt octoate. The octoates of the tested elements, Mn, Cu, Zr, and Fe, were practically inactive individually. Manganese octoate also increased the amount of benzyl alcohol formed in the reaction.

Table 4 contains some data obtained by adding possible catalysts to cobalt octoate. No mixture is as active as cobalt octoate without additives. Only the addition of manganese has a significant effect of increasing the benzyl alcohol formed, which reduces the productivity of the process. However, manganese is identified as an activator for the oxidation of ethylbenzene at levels of 20% of the total catalyst content (Kamyia, 1968).

Table 2 –Effect of some substances in the toluene oxidation reaction.

Promoter or impurity	Mass %	Effect
Acetic acid	2	Avoid the formation of benzyl benzoate, forming benzyl acetate and acetophenone.
Sodium benzoate	0.02 a 0.2	Reduces the production of benzyl alcohol and benzyl benzoate.
Ethanol	4	Inactivate the reaction at the beginning
E.D.T.A	0.04	Deactivate the catalyst (X~10%)
Sodium bromide	0.02	Indifferent in test conditions
T.M.C.A bromide	0.03	Indifferent in test conditions
Sodium fluoride	0.1 a 0.2	Indifferent in test conditions
Sodium pyrophosphate	0.1 a 0.2	Indifferent in test conditions

Table 3 – Evaluation of catalysts alternatives to cobalt octoate

Catalyst	Metal and Mass %	Result
Manganese octoate	0.002% Mn	Slightly active XMAX~5%. ↑ Alc. Benzyl.
Cuper octoate	0.005% Cu	Practically inactive XMAX~1%
Zirconium octoate	0.007% Zr	Practically inactive XMAX~0.2%
Iron octoate	0.004% Fe	Not very active XMAX~3%

Table 4 – Addition of promoters to cobalt octoate catalyst.

Element	Salt and Mass %	Efeito
Manganese	$KMnO_4$ (0.0003% Mn)	↑ Benzyl alcohol. Deactivate by X~14%.
Manganese	Mn octoate Mn (0.002% Mn)	↑ Benzyl alcohol. Deactivate by X~12%.
Chromium	$K_2Cr_2O_7$ (0.0007% Cr)	Indifferent
Chromium	Cr acetate (0.02% Cr)	Deactivates the catalyst by ~7%
Iron	Fe octoate (0.004% Fe)	Strongly deactivates the catalyst
Copper	Cu octoate (0.005% Cu)	Strongly deactivates the catalyst
Zirconium	Zr octoate (0.007% Zr)	Strongly deactivates the catalyst
Molybdenum	Na_2MoO_4 (0.0002% Mo)	Strongly deactivates the catalyst
Cobalt	Co Acetate (0.01% Co).	↓ Benzyl benzoate and ↑ acetophenone

X = conversion of the reaction.

Although zirconium is identified in the literature (Jongsma *et al*., 1980) as an excellent cobalt promoter, in the tests carried out in this project, the use of zirconium salt completely inhibited the reaction. This inhibition has also been noted with octoates of other metals. This may indicate that the raw materials that make up the octoates in the samples used in the tests are inhibitors of the reaction.

The study of this reaction raises new possibilities for the application of soluble catalysts; for example (Liu *et al*., 2021), the liquid phase oxidation of xylenes to terephthalic acid and isophthalic acid seems to be an alternative to obtention of these compounds. More recently (Li *et al*., 2023), the conversion of HMF to FDCA, one possible substitute for terephthalic acid in PETs, was studied.

Conclusions

It was found that it is possible to increase the productivity of benzoic acid in the reaction by increasing the O_2/toluene ratio and reducing the formation of benzyl benzoate and benzyl alcohol, which consume benzoic acid in the reactor and a distillation column through esterification.

In addition, it is also possible to reduce the formation of benzyl alcohol and benzyl benzoate by maintaining the temperature between 135 and 145 °C.

As the conversion rate and extent increase, the amount of benzyl alcohol decreases, and the yield of benzoic acid increases. This fact could be explained by the increasing water in the reaction media, which could cause the hydrolysis of benzyl benzoate.

The yield of benzoic acid increases the sodium benzoate, which reduces the benzyl alcohol and, consequently, the benzyl benzoate, probably because it catalyzes the hydrolysis of the benzyl benzoate.

Acknowledgments

References

Bonnart, J.; Poilane, G. (1968) Production of benzyl alcohol and benzaldehyde. U.S.Pat. 3387036.

Bulushev, A. D. (2004). Partial oxidation of toluene to benzaldehyde and benzoic acid over model vanadia/titania catalysts: role of vanadia species. *Catal. Today*, 96 (4) 195–201. https://doi.org/10.1016/j.cattod.2004.06.143

Del_Olmo A.; Calzada, J.; Nuñez, M. (2017). Benzoic acid and its derivatives as naturally occurring compounds in foods and as additives: Uses, exposure, and controversy. *Critical Reviews in Food Science and Nutrition*, 57(14), 3084-3103. https://doi.org/10.1080/10408398.2015.1087964

Gast, S.; Tuttlies, U.S.; Nieken, U. (2020). Kinetic study of the toluene oxidation in homogeneous liquid phase. *Chemical Eng. Science*, 2017, 115500. https://doi.org/10.1016/j.ces.2020.115500

Gizli, A.; Aytimur, G.; Alpay, E.; Atalay, S. (2008). Catalytic liquid-phase oxidation of toluene to benzoic acid. Chem. Eng. Technol., 31(3), 409–416. https://doi.org/10.1002/ceat.200700140

Hancock, S. (1992). Toluene and xylene and their industrial derivatives, Elsevier.

Jongsma, C.; Laugs, W. (1980). Process for preparing aromatic carboxílic acids. EP 026507.

Kamiya, Y. (1968). Autoxidation of hydrocarbons catalyzed by cobalt and bromine ions. Oxidation of organic compounds – II. *Advances in Chemistry Series*, 76, 193–206.

Li, L.; Yang, S.; Jin, H.; He, G.;, Guo, X.; Ma, L. (2023). The experimental study on the air oxidation of 5-hydroxymethylfurfural to 2,5-furan dicarboxylic acid with Co–Mn–Br system" *Green Processing and Synthesis*, 12(1),20230116. https://doi.org/10.1515/gps-2023-0116

Lyu, Q.; Dong, J.; He, R.; Sun, W.; Zhao, L. (2021). Chemical Engineering Science 232, 116340. https://doi.org/10.1016/j.ces.2020.116340

Maki, T. (1998). Benzoic Acid and Derivatives. *In: Ullmann´s Encyclopedia of Industrial Chemistry - Electronic Release*, John Wiley & Sons.

Noda, S., Kitazono, E., Tanaka, T. *et al*. (2012). Benzoic acid fermentation from starch and cellulose via a plant-like β-oxidation pathway in Streptomyces maritimus. *Microb Cell Fact*, 11, 49. https://doi.org/10.1186/1475-2859-11-49

Partenheimer, W. (1998). Novel catalytic characteristics of the Co/Mn/Br/Cl liquid phase oxidation catalyst. *In: Catalysis of organic reactions*. Marcel Decker.

Poço, J.G.R. (2003) *Melhoria e implementação de novas tecnologias nos processos de fabricação de ácido benzóico e derivados. RT 65584*, IPT.

Shengwei, T.; Liang, B. (2007). Kinetics of the liquid-phase oxidation of toluene by air. Ind. Eng. Chem. Res., 46, 6442-6448. https://doi.org/10.1021/ie070040c

So, Y-M; To, C. T.; Guru, M.M.; Shima, T.; Hou, Z. (2023). Hydrodeoxygenative coupling and transformation of aldehydes at a N2-derived tetranuclear titanium imide/hydride framework. *J. Am. Chem. Soc*. 145 (30), 16906–16912. https://doi.org/10.1021/jacs.3c05525

Takao, M. *et al*. (1984). Preparation of benzaldehyde and benzyl alcohol. JP59134737.

Zhou, Y., Sekar, B. S., Wu, S., & Li, Z. (2020). Benzoic acid production via cascade biotransformation and coupled fermentation-biotransformation. *Biotechnology and Bioengineering*, 117(8) 2340-2350. https://doi.org/10.1002/bit.27366