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Conversion of carbon dioxide to resorcylic acid under ultrasonication by Kolbe–Schmitt reaction

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ABSTRACT

The present work focuses on a new approach for the synthesis of β-resorcylic acid based on Kolbe–Schmitt reaction using carbon dioxide under ultrasonic and mild condition. The Kolbe–Schmitt reaction is a process for the synthesis of β-resorcylic acid (2,4-dihydroxybenzoic acid) from resorcinol in aqueous potassium hydroxide solution with gaseous CO_2. The influences of carbonation time, flow rate of CO_2 and the molar ratio of resorcinol/potassium hydroxide on the yield percentage of resorcylic acid were investigated. The study was assessed with the conventional thermal method (non ultrasonic method) for Kolbe–Schmitt reaction and it was observed that applying ultrasound to save more than 95% and 38.6% energy as shown by energy consumption calculations in bath type and horn type sonicator respectively. β-Resorcylic acid formed was characterized by ^{1}H NMR, ^{13}C NMR, DEPT NMR and FTIR spectroscopy. The amount of CO_2 utilized in the reaction was evaluated from the yield percentage of β-resorcylic acid yield. The maximum yield of resorcylic acid of 30% and 65% was obtained at the resorcinol/potassium hydroxide ratio of 1:3, carbonation time of 150 min and the CO_2 flow rate of 2 L/min in bath type and horn type ultrasonicator, respectively. The applicability of the research work was examined in two different positional isomers of resorcinol under optimum conditions.

1. Introduction

Carbon dioxide, more than 30 billion tons of which are annually released to the atmosphere, is believed to be responsible for global warming and consequent climate change [1]. From the viewpoint of environmental protection and resource utilization, it is important to transform CO_2 into useful chemicals efficiently. In fact, it may be relevant to both the carbon dioxide mitigation and the development of benign synthesis. Carbon dioxide is an end product of many industrial and biological processes [2]. It is well known that the CO_2 is a very stable gas and unreactive but plants are utilizing it in the photosynthesis of carbohydrate [3]. To find a way to make chemicals from CO_2 synthetically would be an environmentally benign route. Various existing utilization technologies for the optimum CO_2 utilization were fixation of CO_2 into organic compounds (production of various chemical products), microalgae biomass production (pond and bioreactor production), supercritical CO_2 extraction technology and CO_2 reforming of methane [3]. The value-added products that can be produced from these four main technologies are organic carbonates (linear, cyclic or polycarbonates), carboxylates (formic acid, oxalic acid, etc.), resorcylic acid, salicylic acid and urea which can be used in pharmaceutical, chemical or nutritional products. The feasibility of these processes was evaluated according to their thermodynamics, energy, production rates and yields, product values and economics.

The Kolbe–Schmitt synthesis is a traditionally used carboxylation reaction for phenolic cores, which enables the introduction of a carboxylic group by an electrophilic substitution and Kolbe–Schmitt reaction remains the standard commercial method for the preparation of aromatic hydroxy acids [4,5]. An example of important industrial synthesis under conventional conditions is the aqueous Kolbe–Schmitt synthesis of β-resorcylic acid. β-Resorcylic acid is an industrially produced by the reaction of resorcinol with an aqueous solution of potassium hydroxide in the presence of a carbon dioxide. The aromatic hydroxy carboxylic acids are used in the pharmaceutical and cosmetic industry as well as in the production of dyes and plastics [6]. Apart from conventional methods, resorcylic acid synthesis has also been reported by various researchers. Benaskar et al. investigated the resorcylic acid synthesis in a microwave assisted reactor and obtained a yield of 40% [7], Krtschil et al. described about the process carried out by means of capillary reactor with yield of 38% [8], Benaskar et al.,

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Hessel et al. elaborated Kolbe–Schmitt reaction on conventionally heated oil bath reactor and reported the yield of 47% [9] and Hessel et al. and Hale et al. enlighten the aqueous Kolbe–Schmitt synthesis of β-resorcylic acid under high temperature and high pressure with the yield of 44% and 23% [10]. The conventional reaction conditions in the preparation of organic compounds are also harsh for most of these reactions and some are even related to tedious work-up procedures. Therefore, there is an obvious need to develop an efficient synthetic method that would synthesize valuable organic compound under milder conditions and in an environmentally benign manner.

Application of ultrasound in organic transformation has proved to be an important tool in enhancing reaction rates and improving yields [11]. It promotes the reaction under milder conditions where drastic conditions are required conventionally. Ultrasound has been used to accelerate the rates of numerous chemical reactions; intense ultrasonic waves traveling through liquids generate small cavities that enlarge and implode, creating tremendous heat. These extreme conditions provide an unusual chemical environment [12].

The introduction of a strong acoustic field to an aqueous solution results in the generation of cavitation micro bubbles. The growth and collapse of these micro bubbles focuses and transfers energy from the macro-scale (acoustic wave) to the micro-scale (vapor inside the bubbles) producing extremely high localized pressures and temperatures. This unique energy focusing process generates highly reactive free radicals that have been observed to significantly enhance chemical processing [13]. In that focus the study has been carried out in the synthesis of resorcylic acid in an aqueous medium under an ultrasonic environment.

In this work, a variant of the Kolbe–Schmitt synthesis which uses ultrasonic environment to get milder conditions instead of applying energy intensive high pressure and high temperature in the carboxylic acid production was investigated and which would be a greener pathway. To the best of our knowledge, no ultrasonic dependent syntheses are available in the literature for the carboxylation of resorcinol in an aqueous solution. In this paper, we present a distinctive utilization of a carbon dioxide in the conversion of resorcinol to β-resorcylic acid at ambient temperature and pressure under ultrasonication procedure as shown in Fig. 1.

2. Materials and methods

All chemicals used in the present study were of analytical grade. Resorcinol and potassium hydroxide were obtained from Merck, India and used as received. Research grade carbon dioxide gas, 99.9%, was purchased from Supreme Engineering Services, India, and used as a source of carbon dioxide without further treatment. Diethyl ether and sodium bicarbonate were purchased from Merck, India and used for the extraction of resorcylic acid. All experimental solutions were prepared using demineralised water.

2.1. Experimental setup

The experimental reactor setup is shown in Fig. 2. All reactions were carried out in a double necked round bottomed flask of 250 mL capacity that was dried prior to use. Resorcinol and KOH were added in the round bottomed flask. One neck of the reactor was sealed with condenser and carbonated through another neck for a required time under ultrasonication (Model Bandelin sonorex RK52-Germany) (bath type sonicator). Then it was exposed to a continuous flow rate of carbon dioxide gas at a certain flow rate with the help of a rotameter and the reactions were continued for a required time. After completion of the reaction the contents of the vessel were then taken out and subjected to analysis. Heilscher UP400S ultrasound technology (horn type sonicator) with 20 kHz frequency was also used to compare the effects of sonication amplitude on the synthesis of resorcylic acid.

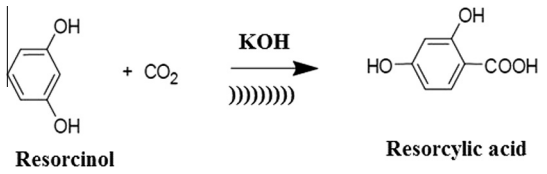

Fig. 1. Scheme of the synthesis of β-resorcylic acid (2,4-dihydroxybenzoic acid) from resorcinol.

2.2. Isolation and purification

In the Kolbe–Schmitt synthesis, the product was isolated by ether extraction from mother liquor followed by shaking with an aqueous solution of sodium bicarbonate. The aqueous layer was acidified with hydrochloric acid and then extracted with ether and subsequently ether was evaporated parting the product of resorcylic acid [14].

2.3. Analytical techniques

The reactor content was collected and isolated using ether extraction, identified the compound using alumina coated TLC plates and then subsequently characterized by FTIR were recorded on Bruker, 4000–450 cm^{-1} to identify the functional group in the compound, ^{1}H NMR were obtained with Bruker Avance III, 500 MHz to observe the proton–proton coupling; ^{13}C NMR were recorded on Bruker Avance III, 125 MHz to study the carbon–carbon stretching and DEPT (Bruker Avance III, 45 MHz) analyses to obtain the sub spectra of ^{13}C NMR spectrum which helps to predict the absence of quaternary carbon.

3. Results and discussion

The study focuses on sonication dependent synthesis of resorcylic acid by the activation of the CO_2 molecule in the reaction towards the development of environmentally benign route. Ultrasound has been proven to be a potentially useful tool for intensification of carbonation processes. Due to enhanced mixing, particle breakage and removal of passivating layers it was possible to accelerate the reaction kinetics, and achieve greater carbonation extent in shorter times and greater maximal conversion [15].

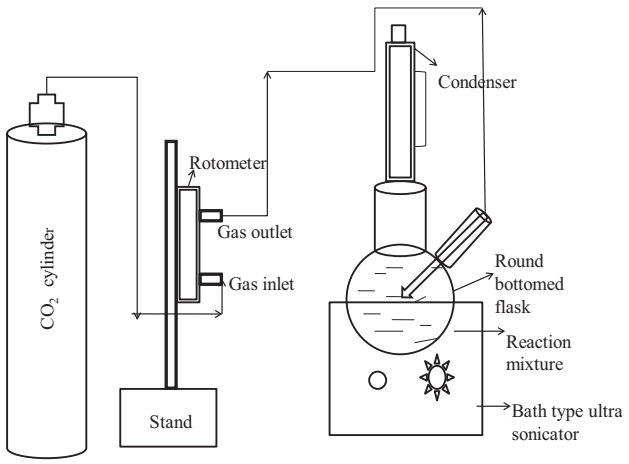

Fig. 2. Schematic diagram of the reactor.