



Hydrodynamic cavitation for the enhancement of toluene disproportionation; study of the products distribution

Jing-Mei Liu^a, Feng-Yun Ma^{a,*}, Yong-Hui Zhu^a, Yu-Fang Ye^a, Ya-Qiong Liang^a, Yue-E Liu^a, Xian-Yong Wei^b

^a Key Laboratory of Coal Clean Conversion & Chemical Engineering Process, Xinjiang Uygur Autonomous Region, College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, China

^b Key Laboratory of Coal Processing and Efficient Utilization, Ministry of Education, China University of Mining & Technology, Xuzhou 221116, Jiangsu, China

ARTICLE INFO

Keywords:

Hydrodynamic cavitation
Toluene
Disproportionation
P-xylene

ABSTRACT

In a toluene-water mixture, toluene disproportionation can occur under very gentle conditions if enhanced by a hydraulic cavitation field. Using a single factor approach, the effects of toluene concentration, ethanol and H₂O₂ addition, final reaction temperature, and pH on toluene conversion and yields of products in the organic phase were investigated. The optimal reaction conditions for *p*-xylene (PX), an objective product, were 12.5% (v/v) concentration of toluene and ethanol, final reaction temperature of 50 °C, pH of 9, and a H₂O₂ addition of 2.5% (v/v). Under such conditions, the toluene conversion reached 19.66%, and yields of benzene, alkyl cycloalkanes, and alkyl aromatic hydrocarbons were 2.70%, 2.64%, and 14.32%, respectively. Particularly, yields of PX, *o*-xylene (OX), and ethylbenzene were 8.56%, 4.06%, and 1.70%, respectively. A reaction mechanism was proposed and validated via both UV spectroscopy of the aqueous-phase products and material balance for the process.

1. Introduction

Toluene is generally found among aromatic hydrocarbons from various sources like products of catalytic reforming and steam cracking of petroleum fractions, direct coal liquefaction products, coal aromatics, etc. [1–3]. However, compared to benzene and xylene, industrial applications of toluene are extremely limited. These limitations result in an excessive availability of toluene, while the market suffers from shortages of benzene and xylene, especially PX. Current prices of toluene (about \$600/t), benzene (\$730/t), and PX (\$805/t) differ greatly. Hence, the technology focusing on toluene disproportionation into benzene and PX has always been an important research area in the petrochemical industry.

For toluene disproportionation, the traditional technologies are Xylene-Plus, Tatoray (toluene-disproportionation and C₉ aromatics alkyl transfer), low temperature toluene disproportionation (LTDP), mobil toluene disproportionation (MTDP), and mobil selective toluene disproportionation (MSTDP) [4]. These methodologies are well studied and they present several problems: processes are lengthy and complex, reaction temperatures are high, PX selectivity is low, conditions are hard, energy and water consumption is high, and catalysts have poor stability [5]. Therefore, solving these problems still remains a central

issue.

Hydrodynamic cavitation technology can improve the results of many organic reactions even under mild conditions and has been increasingly investigated [6–14].

Ambulgekar et al. reported that under hydrodynamic cavitation, toluene was oxidized to benzoic acid at 35 °C for 3 h with KMnO₄ as catalyst with a 44% yield [6]. Subsequently, under the optimized reaction conditions, xylenes were oxidized to the corresponding *ortho*-, *meta*-, or *para*-aryl carboxylic acid, and the yield of terephthalic acid was 60% [7]. Maddikeri et al. used Venturi-tube cavitation to intensify the transesterification reaction of waste cooking oil, yield 90% of biodiesel at 45 °C and 0.3 MPa, obtain an oil-to-methyl acetate ratio of 1:12 with 1% methanol as catalyst [8]. V. L. Gole et al. improved the synthesis of methyl esters with a single-orifice-type cavitation tube at parameters of 50 °C–65 °C, 0.3 MPa, a methanol-to-sulfuric acid ratio of 1:3 and 1 h to obtain a 91.8% yield [9]. Ye et al. enhanced a soybean oil distillate esterification-deacidification reaction in a throttle hydraulic cavitation reactor with conditions of a pressure of 0.3 MPa, oil-to-alcohol ratio of 5:1 (v/v), temperature range of 55 °C–60 °C and 3 h. Both esterification conversion and vitamin-E yield were 99% [10]. Chen et al. enhanced a soybean oil epoxidation reaction using a porous orifice plate cavitation reactor, and obtained a conversion rate and

* Corresponding author.

E-mail address: ma_fy@126.com (F.-Y. Ma).

epoxidation selectivity of 98% and 81%, respectively, at reaction conditions of 0.5 MPa, 70 °C, and 6 h [11]. Using a Venturi tube combined with porous orifice plates, Ye et al. increased acenaphthene content in creosote oil by 30.63% [12]. The optimal conditions were water addition of 17.5 wt%, 0.3 wt% of Fe^{2+} , in a FeSO_4 solution with pH = 1 and 75 °C. Manickam Sivakumar et al. enhanced the degradation of rhodamine B dye solution using multiple holes orifice plates [15]. P. Senthil Kumar et al. studied the decomposition of an aqueous KI solution with a 50 L hydrodynamic cavitation device, and compared it with acoustic cavitation. Results indicated that manipulation of the throttling device and the operation conditions increased the iodine liberation rate three times compared to acoustic cavitation at equivalent power dissipation rates [16]. Using a liquid whistle hydrodynamic cavitation reactor, Shridharan Parthasarathy et al. prepared palm oil based oil-in-water submicron emulsions in the presence of Tween 80 [17]. Siah Ying Tangand et al. [18] produced submicron scale (~ 600 nm) highly stable W/O/W multiple emulsions containing ferrous fumarate.

Hydrodynamic cavitation clearly possesses many advantages for the improvement of organic reactions such as simple process, mild condition, easy control, etc. However, disproportionate conversion of toluene into benzene and PX, which is enhanced by hydrodynamic cavitation, has not been reported. The aim of this work is to study this disproportionation reaction in water at low temperature using hydraulic cavitation. The effects of toluene concentration, reaction final temperature, ethanol and H_2O_2 addition, and pH were investigated. Product yields in the organic phase were also analyzed, and the reaction improvement mechanism was discussed. A new viable green way for disproportionate conversion of toluene into benzene and xylene, particularly into PX, was reported.

2. Experimental

2.1. Devices and reagents

As shown in Fig. 1(A), the experimental device comprises the reaction and cooling system. The former contains a cavitation reactor, a vertical tank containing the reaction materials, a gear pump and pipeline; and the latter comprises a cold trap and a vertical-tank jacket. In the reaction system, the cavitation tube, whose internal structure and parameters are shown in Fig. 1(B), consists of two porous orifice plates and a Venturi tube. The inlet of the cavitation tube is connected to the pipe outlet. During the reaction process, two-thirds of the tube, including the outlet, must be immersed in the solvents to a total volume of 4 L. There are a feed inlet and a hole on the top of the vertical-tank, where a thermocouple is inserted to detect the reaction temperature at any time. The material outlet is at the bottom of the tank that is fitted to one end of a three-way pipe. Another end of the tee connects to the drainage tube, and the third to the inlet pipe of the pump. A pressure gauge is installed in the upstream line of the tube to measure the reaction pressure, which is maintained at 2.4–2.6 MPa during the experimental process. In the cooling system, the cooling medium is a 1:1 (v/v) mixture of water and ethylene glycol that circulates between the cold-trap and tank jacket. The cold-trap temperature was set to -15 °C.

All of the chemicals used in experiment, toluene, ethanol, H_2O_2 , H_2SO_4 , and NaOH are of analytical grade. Distilled water was used.

2.2. Reaction procedure

Firstly, the cooling system was initiated to decrease the temperature from ambient to -15 °C. Then the feedstock was slowly poured into the tank through a funnel. The outlet valve was closed and the pump was opened. The feedstock began to circulate and react in the system, and the materials temperature continuously increased with reaction time. After the reaction temperature reached a predetermined value, the pump was closed and the reaction stopped. The outlet valve was then

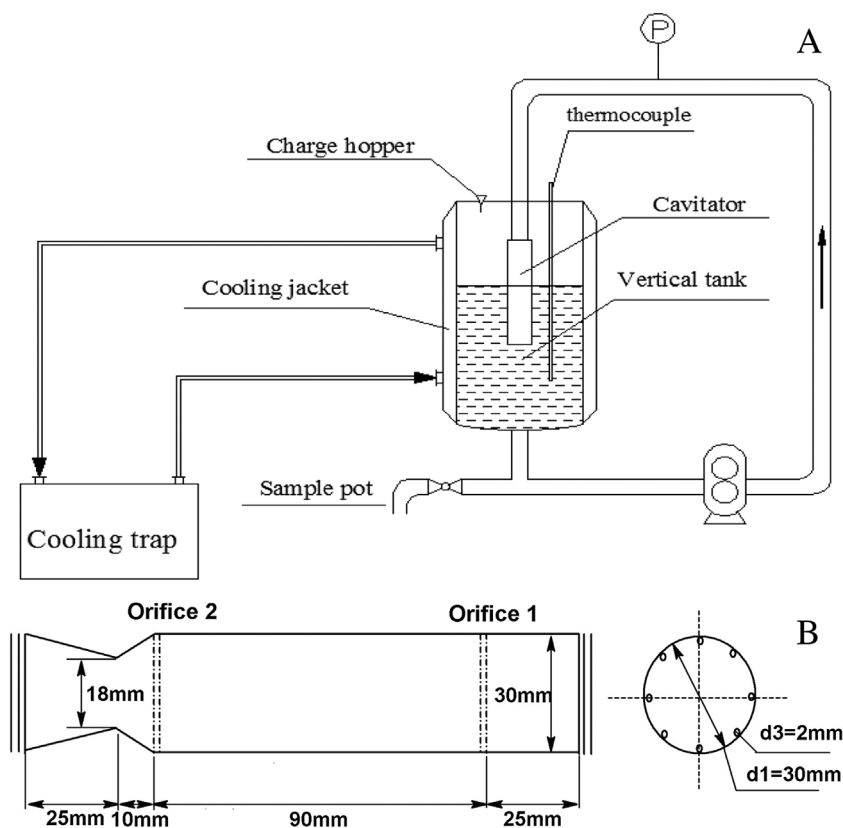


Fig. 1. Scheme of the hydrodynamic cavitation device.

Download English Version:

<https://daneshyari.com/en/article/7088829>

Download Persian Version:

<https://daneshyari.com/article/7088829>

[Daneshyari.com](https://daneshyari.com)