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Application of ultrasonic spraying in preparation of *p*-cymene by industrial dipentene dehydrogenation

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ABSTRACT

Preparation of *p*-cymene in a pilot equipment using ultrasonic spraying of raw material industrial dipentene (DP) was studied. By comparison with common spraying, it was found that ultrasonic spraying could improve DP dehydrogenation process. The running temperatures of preheater and spray room were all relative lower (10–25 and 100–150 °C). The *p*-cymene yields in ultrasonic spraying mode were higher with 2.45–6.23% than those in common spraying mode at 210–270 °C. The *p*-cymene yields in ultrasonic spraying mode were higher with 0.31–1.10% than those in common spraying mode at 280–310 °C. The yield of *p*-cymene was up to 99.25% in the condition of reactor temperature 310 °C, flow rate of DP 4 L/h, nitrogen flow rate 2 L/min based on Pd/C catalyst and ultrasonic spraying.

1. Introduction

p-Cymene is an important chemical widely used for syntheses of *p*-cresol, *p*-hydroxy benzaldehyde, *p*-isopropyl benzaldehyde, *p*-isopropyl benzoic acid, *p*-methyl acetophenone, raspberry ketone, and polycyclic musk compounds, *etc.* [1,2]. A typical method for preparation of *p*-cymene is catalytic dehydrogenation of DP which is a mixture of monocylic terpenes as the by-product from the chemical processing of turpentine oil in China [3]. The literature survey showed that more attention was paid to the preparation and application of catalysts for dehydrogenation of DP or its single component mostly at laboratory scale [4–8]. Few studies focused on engineering or industrialization development of manufacture of *p*-cymene from DP. According to our previous research work [9], changing the aggregation state from liquid to gas of DP or related feedstock in a large scale is one of the key techniques to a catalytic reaction [9]. Unsuitable method to turn DP into gas could bring several disadvantages such as high-energy consumption, coking of feedstock, blocking of spray nozzle, incomplete reaction, destroying or inactivation of catalyst, *etc.*

Application of ultrasounds in different chemical processes became an attractive technique in recent years [10,11]. The use of ultrasonic spraying has been investigated for water atomization, air humidification, dustproof, spraying dryness, burning of fuel oils, and preparations of nano-powder, porous powder, microsphere, thin film or thin film coating, *etc.* [12–16], but not to chemical processes. The liquids flowing through the ultrasonic spray nozzle vibrating at high-frequency ends up into micro-sized liquid droplets or mist. The liquid droplets, the finest they are, the easier would be evaporated in the nitrogen flow at an appropriate temperature. In order to acquire knowledge regarding the ultrasonic spraying versus common spraying systems, a pilot equipment operable with ultrasonic spraying as well as a common spraying to enhance the evaporation of DP for catalytic preparation of *p*-cymene was designed, built and operated. The production capacity of *p*-cymene in the pilot plant presented in this paper for both ultrasonic and common spraying was 20 tons per year.

2. Method

2.1. Reagents and materials

DP which contains monocylic terpenes over 91.0% was purchased from Suzhou Chemical Synthesis Co. Ltd. The Pd/C catalyst containing 4.0–5.0% Pd on activated carbon (cylindric granule, ϕ3 mm × *L*6–10 mm) was supplied by Zhuzhou Sonben Forest

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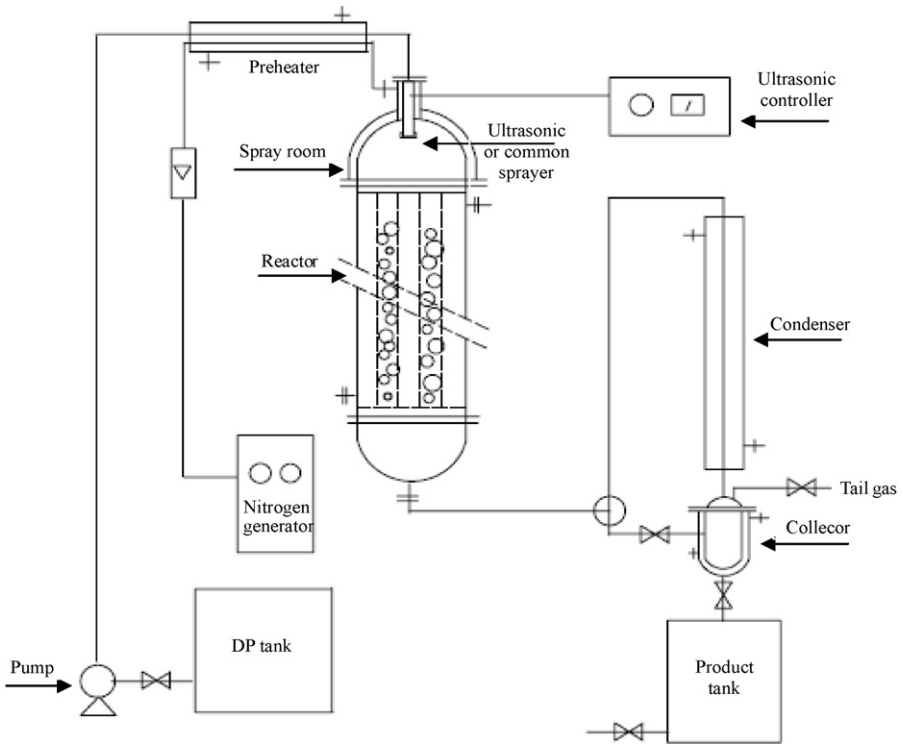


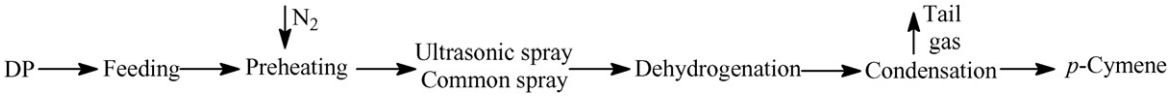
Scheme 1. Equipment of DP dehydrogenation using ultrasonic or common spraying.

Chemical Co., Ltd. Nitrogen was produced by nitrogen generator in flow rate of 0–3.0 L/min and content of 99.9%.

2.2. Experimental procedure

The continuous equipment for preparation of *p*-cymene with 20 tons per year capacity was designed by Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry in Nanjing, China [17–19]. The equipment includes: DP tank, pump, nitrogen generator, preheater, spray room, reactor, condenser, collector, and product tank (see Scheme 1). The pump flow rate for feeding DP could be turned from 0 to 10 L/h. The temperature range of preheater, spray room, and reactor, could be controlled by heat transfer oil from 10 to 150 °C, 100 to 250 °C, and 150 to 350 °C, respectively. The temperatures of condenser and collector were all controlled and kept below 30 °C by a cooling fluid. Inside reactor were three columns filled with total 500–1000 g Pd/C catalyst.

Either ultrasonic sprayer or common sprayer could be installed into the spray room. The ultrasonic sprayer is produced by Hangzhou Success Ultrasonic Equipment Co. Ltd., and has a spray circular cone shape nozzle for spraying. By vibration of ultrasonic transducer with 30 kHz frequency and 50–70 W running power, the liquid DP is transformed into tiny droplets, a mist. The common sprayer has a hole for spraying in diameter of 0.05–1.0 mm. The procedures for preparing *p*-cymene by ultrasonic or common spraying are having the following scheme.



Nitrogen from nitrogen generator was continuously blown into preheater at a flow rate of 2.0 L/min. DP was continuously injected into preheater from DP tank by a metering pump (injector pump). The preheated DP was sprayed by common sprayer while unheated DP by ultrasonic sprayer, mixed with nitrogen to vaporize in the spray room. The gasified DP was dehydrogenated to *p*-cymene over the Pd/C catalyst in the pure nitrogen atmosphere into reactor. The products were collected into products tank after being cooled in condenser and collector. The tail gas containing nitrogen, hydrogen, and other non-condensable gas released out of the collector by a pipeline. The obtained products in different conditions were analyzed by gas chromatography.

2.3. Analysis

As analytical equipments a gas chromatograph (Shimazdu GC-2014) and a gas chromatograph–mass spectrometer (Agilent 6890N) were employed. The GC was equipped with Rtx-5 capillary column (0.25 mm × 30 m × 0.25 μm) and a FID detector. The temperature profile of column was: holding 2 min at 70 °C, rising temperature at the rate of 3 °C/min to 130 °C, and then at the rate of 10 °C/min to 180 °C. The carrier gas was nitrogen and split ratio was 50:1. The content of every component was calculated according to area fraction of the response peak based on total peaks in gas chromatogram.

The GC–MS was equipped with Network GC system containing a column of HP-5 (0.25 mm × 30 m × 0.25 μm), Agilent 5973 Network Mass Selective Detector, and Agilent 7683 Series Injector. The temperature profile of column was: holding 10 min at 70 °C, rising temperature at the rate of 2 °C/min to 100 °C, and then at the rate of 10 °C/min to 280 °C. The carrier gas was helium and split ratio was 100:1. EI mode was used for ionization. Identification of compounds was mainly according to auto-comparison of NIST2002 MS library with the spectra of every component.

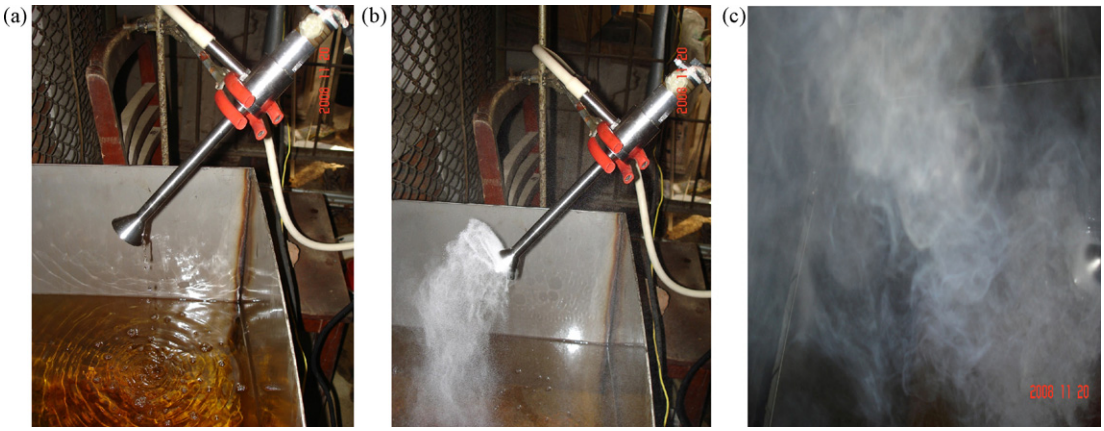


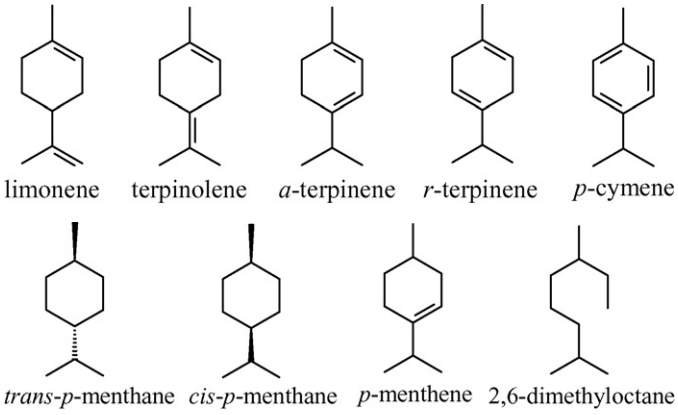
Fig. 1. Ultrasonic spraying of DP at room temperature; (a) no ultrasound; (b) beginning of ultrasonic spraying; (c) steady state ultrasonic spraying.

3. Results and discussion

3.1. Constituents of DP and its dehydrogenation product

The GC–MS and GC analyses of DP used in this study shown 91.36% mixture of monocylic terpenes. The main components are: limonene 30.32%, terpinolene 31.35%, α-terpinene 7.55%, γ-terpinene 6.40%, and *p*-cymene 12.87%. It also contains small amount of camphene, *p*-menthene, β-phellandrene, and carene.

The main catalytic dehydrogenation product of DP was *p*-cymene. However, some hydrogenation by-products result from reaction including *trans*-*p*-menthane, *cis*-*p*-menthane, *p*-menthene, and 2,6-dimethyloctane. Between common and ultrasonic spraying no different compounds were observed in the outcome.



3.2. Ultrasonic spraying of DP

The ultrasonic spray nozzle has a specific design: the DP is feed throughout a tube directly inside the horn from where the liquid reach the conical shape surface that by vibrations atomizes the liquid. The diameter of the tube outlet of ultrasonic spray nozzle is 3 mm which could produce 2–5 mm diameter droplets at different flow rates. Before setting the ultrasonic power on, the liquid passed through the spray nozzle and fall as 2–5 mm diameter droplets which are estimated by vision (Fig. 1(a)). When the ultrasonic power sets on, the droplets were immediately broken to white micro-droplets on the surface of spray nozzle. The micro-droplets slowly descend down (Fig. 1(b)). After running 2–3 min, the micro-droplets became a white mist. They all steadily floated and ascended in the air (Fig. 1(c)). The above experimental results were better than those estimated in the design stage.

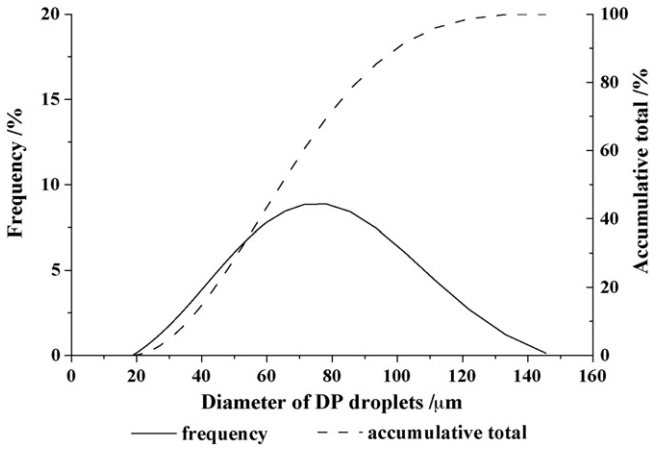


Fig. 2. Size distribution of DP droplets by ultrasonic spraying (from Winner 313 Laser particle size analyzer).

The droplets size distribution is shown in Fig. 2.

The average size of ultrasonic created droplets is 66.266 μm. These droplets are quickly evaporated when they reach the spray room due to the nitrogen and spray room temperatures. The difference from common spraying is that in the ultrasonic spraying the DP is pumped into the spraying device at room temperature (10–25 °C) while for common spraying it is preheated to 100–150 °C.

3.3. Comparison of ultrasonic spraying with common spraying

Both spraying techniques could realize spraying or atomization and help vaporization of DP. The temperature of preheater in ultrasonic spraying mode was only 10–25 °C (means no heating), while for common spraying mode was 100–150 °C. The running temperature range of spray room in ultrasonic spraying mode and common spraying mode were respectively 100–150 and 200–250 °C. For both spraying methods the nitrogen flow rate was 2 L/min and of DP 4 L/h. Table 1 below summarizes the temperature profiles for both spraying methods. It is obvious that using ultrasonic spraying

Table 1
The temperatures profiles for both spraying methods.

	Ultrasonic spraying	Common spraying
Preheater temperature	10–25 °C	100–150 °C
Spray room temperature	100–150 °C	200–250 °C
Energy consumption	Low	High

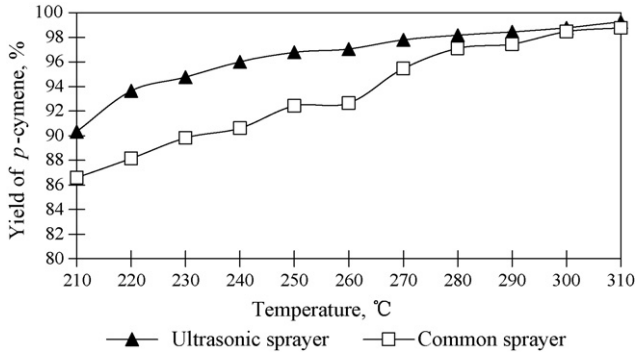


Fig. 3. Influence of spraying mode on DP dehydrogenation.

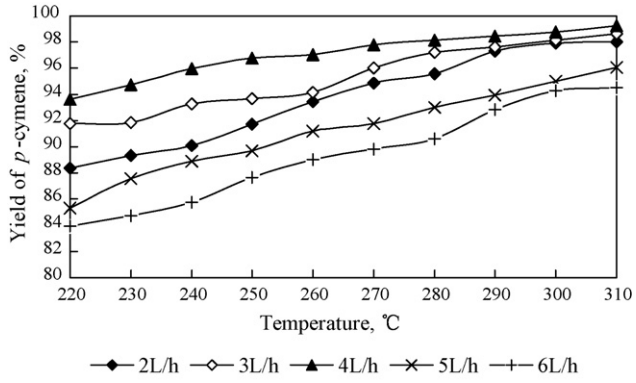


Fig. 4. Influence of DP flow rate on *p*-cymene yield by ultrasonic spraying.

(50–70 W power) is less energetically than high temperature preheater for common spraying system.

The catalytic reactor temperature was in the range of 210–310 °C. The *p*-cymene yields in ultrasonic spraying mode at different reactor temperatures were: 90.33% (210 °C), 93.65% (220 °C), 94.75% (230 °C), 95.99% (240 °C), 96.77% (250 °C), 97.04% (260 °C), 97.80% (270 °C), 98.16% (280 °C), 98.43% (290 °C), 98.77% (300 °C), and 99.25% (310 °C). The *p*-cymene yields in common spraying mode at different reactor temperatures were: 86.59% (210 °C), 88.16% (220 °C), 89.82% (230 °C), 90.961% (240 °C), 92.42% (250 °C), 92.65% (260 °C), 95.46% (270 °C), 97.09% (280 °C), 97.44% (290 °C), 98.46% (300 °C), and 98.76% (310 °C). Their relationship curves could be seen in Fig. 3.

As one can see in Fig. 3, the yield of *p*-cymene is higher at reactor's temperatures ranging between 210 and 270 °C. It means that the ultrasonic spraying mode has advantage over the common spraying mode, especially in relative lower reactor temperature. These differences are due to the much lower size of the droplets generated ultrasonically. This facilitates DP evaporation in the nitrogen gas and therefore much uniform flow goes throughout the catalytic bed. This is easier to see when the reactor's temperature goes in the range of 280–310 °C. The higher the reactor's temperature, the higher the reaction rate, diminishes therefore, the role of droplets size, leveling the yields regardless the spray method.

The *p*-cymene yields are better up to 270 °C. Over this temperature the yields are quite similar. The *p*-cymene yields in ultrasonic spraying mode were higher with 2.45–6.23% than those in common spraying mode at 210–270 °C. The *p*-cymene yields in ultrasonic spraying mode were higher with 0.31–1.10% than those in common spraying mode at 280–310 °C. The yields of *p*-cymene by common spray at 280–310 °C have been over 97% which are near to theoretical yield (100%), so the ultrasonic spray improvement at higher temperature is not obvious to the yield. The improvement rate is, of course, impossible to be out of theoretical value. On the other hand, it means reaction temperature is the key factor influenced catalytic dehydrogenation of DP. The ultrasonic spraying is only partial improvement for the total preparation process.

3.4. Effect of DP flow rate

The experimental results of *p*-cymene yield at different DP flow rates (2, 3, 4, 5, and 6 L/h), different reactor temperature (ranging from 220 to 310 °C) and 2 L/min nitrogen flow rate are shown in Fig. 4. The yields of *p*-cymene were increased synchronously with the increasing of temperature by ultrasonic spraying. The DP flow rate was the second key factor on DP dehydrogenation besides reactor temperature. The sequence of DP flow rate which affects the yield of *p*-cymene was 4 L/h > 3 L/h > 2 L/h > 5 L/h > 6 L/h (see Fig. 3). It is concluded that DP flow rate of 4 L/h was the suitable and reasonable condition for above designed equipment in this study. According to our GC analytical results, the contents of by-products such as *trans*-*p*-menthane, *cis*-*p*-menthane, and *p*-menthene in crude products of DP dehydrogenation at 4 L/h DP flow rate were lower than those at 2, 3, 5, or 6 L/h DP flow rate. This means DP flow rate must be matched with the size of DP dehydrogenation equipment.

4. Conclusion

Ultrasonic spraying could replace common spraying with improving yields on catalytic dehydrogenation process of DP. The running temperatures of preheater and spray room in ultrasonic spraying mode were low. The *p*-cymene yields in ultrasonic spraying mode were higher with 2.45–6.23% than those in common spraying mode at 210–270 °C. The *p*-cymene yields in ultrasonic spraying mode were higher with 0.31–1.10% than those in common spraying mode at 280–310 °C. The yield of *p*-cymene was up to 99.25% in the condition of reactor temperature 310 °C, flow rate of DP 4 L/h, nitrogen flow rate 2 L/min based on Pd/C catalyst and ultrasonic spraying.

We plan to use the designed equipment containing ultrasonic sprayer to research gas phase catalysis reaction of other turpentine derivatives or liquid biomass resources with similar processes in next step.

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References

[1] Q.G. Zhang, L.W. Bi, Z.D. Zhao, C.Y. Bo, D.M. Li, Y. Gu, J. Wang. Research progress in preparation and application of *p*-cymene. Modern Chemical Industry (*Xiandai Huagong*) 28 (supplement) (2008) 401–406 (in Chinese).
[2] K.A.D. Swift, Catalytic transformations of the major terpene feedstocks, Topics in Catalysis 27 (2004) 143–155.
[3] L.W. Bi, X.Z. Liu, Z.D. Zhao, P.X. Xu, F.X. Chu, Study on dehydrogenation and cracking of industrial dipentene and analysis of the reaction products, Chemical Industry Times (*Huagong Shikan*) 17 (1) (2003) 30–33 (in Chinese).
[4] P. Lesage, J.P. Candy, C. Hirigoyen, Selective dehydrogenation of dipentene (*R*-(+)-limonene) into para-cymene on silica supported palladium assisted by α-olefins as hydrogen acceptor, Journal of Molecular Catalysis A: Chemical 112 (1996) 431–435.
[5] D.C. Liu, Z.Q. Sun, Q.H. Guo, Study on preparation process of *p*-cymene with gas-phase catalytic dehydrogenation of industrial dipentene, Fine Chemicals (*Jingxi Huagong*) 15 (6) (1998) 42–45 (in Chinese).

[6] D. Buhl, D.M. Roberge, W.F. Holderich, Production of *p*-cymene from α-limonene over silica supported Pd catalysts, Applied Catalysis A: General 188 (1999) 287–299.
[7] M.A. Martin-Luengo, M. Yates, M.J.M. Domingo, B. Casol, M. Iglesias, M. Esteban, E. Ruiz-Hitzky, Synthesis of *p*-cymene from limonene, a renewable feedstock, Applied Catalysis B: Environmental 81 (2008) 218–224.
[8] C.w. Zhao, j.x. Gan, b. Fan, Z.P. Cai, P.J. Dyson, Y. Kou, Aqueous-phase biphasic dehydroaromatization of bio-derived limonene into *p*-cymene by soluble Pd nanocluster catalysts, Journal of Catalysis 254 (2008) 244–250.
[9] L.W. Bi, Z.D. Zhao, X.Z. Liu, D.M. Li, J. Wang, Comparison on synchronous and asynchronous reaction of dehydrogenation and cracking of dipentene, Journal of Chemical Industry of Forest Products (*Linchan Huagong Tongxun*) 38 (1) (2004) 5–8 (in Chinese).
[10] T.J. Mason, J.P. Lorimer, Applied Sonochemistry: The Uses of Power Ultrasound in Chemistry and Processing, Wiley-VCH Verlag GmbH, Weinheim, 2002.
[11] C. Stavarache, M. Vinatoru, Y. Maeda, H. Bandow, Ultrasonically driven continuous process for vegetable oil transesterification, Ultrasonics Sonochemistry 14 (2007) 413–417.
[12] W.H. Suh, K.S. Suslick, Magnetic and porous nanospheres from ultrasonic spray pyrolysis, Journal of the American Chemical Society 127 (2005) 12007–12010.
[13] N.H. Lee, J.H. Kim, H.J. Oh, S.J. Kim, *In situ* preparation of highly crystallized ZnO nanopowders by ultrasonic spraying combustion method, Solid State Phenomena 121–123 (2007) 1269–1272.
[14] S.E. Skrabalak, K.S. Suslick, Porous carbon powders prepared by ultrasonic spray pyrolysis, Journal of the American Chemical Society 128 (2006) 12642–12643.
[15] F.A. Mahmoud, G. Kiriakidis, Nanocrystalline ZnO thin film for gas sensor application, Journal of Ovonic Research 5 (2009) 15–20.
[16] W.H. Suh, A.R. Jang, Y.H. Suh, K.S. Suslick, Porous, hollow, and ball-in-ball metal oxide microspheres: preparation, endocytosis, and cytotoxicity, Advanced Materials 18 (2006) 1832–1837.
[17] L.W. Bi, Z.D. Zhao, Q.G. Zhang, D.M. Li, Y. Gu, J. Wang, X.Z. Liu, The method and device for production of *p*-cymene, Chinese Patent (*Faming*) ZL 200910029138.3, from January 7th (2009).
[18] L.W. Bi, Q.G. Zhang, Z.D. Zhao, D.M. Li, Y. Gu, J. Wang, X.Z. Liu. The device for production of *p*-cymene, Chinese Patent (*Shiyongxinxing*) CN 200920038552.6, from January 7th (2009).
[19] L.W. Bi, Q.G. Zhang, Z.D. Zhao, D.M. Li, Y. Gu, J. Wang, X.Z. Liu. The device for production of *p*-cymene by ultrasonic atomization and gasification, Chinese Patent (*Shiyongxinxing*) ZL 200920039462.9, from April 10th (2009).