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硕 士 学 位 论 文

十二烷基二苯醚磺酸钠清洁生产工艺探索及其性能研究

Studies on Cleaner Production Technology and Performance of Dodecyl Diphenyl Ether Sodium Disulfonate

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摘要

烷基二苯醚磺酸盐（ADPEDS）作为一种性能优异的多功能性表面活性剂，其具有一系列优良的性能，除用作特效高性能洗涤剂之外，在诸多工业领域具有重要而广泛的应用，如在三次采油工业中用作高性能驱油剂、在乳液聚合工业中用作高性能乳化剂和稳定剂、在印染工业中用作优良的均染剂及在其他工业领域中的应用等。该产品在国外已实现了工业化生产，其关键生产技术被国外公司所垄断。目前国内对该产品的研究主要处于实验室研究阶段，尚无工业化生产报道，产品需求主要依赖国外进口。因此，开展对该类表面活性剂的生产工艺研究具有重要的意义。

本论文首先对十二烷基二苯醚磺酸钠（DDES）清洁生产工艺进行了探索，通过优化其合成工艺，确定了较佳的反应条件，然后对所合成的系列产品的性能进行了测试与分析，最后设计了年产 1200 吨的单十二烷基二苯醚磺酸钠的工业化方案，具体研究内容如下：

（1）以二苯醚和十二醇为原料，固体酸为催化剂，合成单十二烷基二苯醚（SAPE）；然后对 SAPE 进行磺化、中和得到系列单十二烷基二苯醚磺酸钠（SAPS）。综合考虑各种因素对反应的影响，确定合成 SAPE 的较佳反应条件为：以固体酸为催化剂，二苯醚与十二醇的摩尔比为 4∶1，反应温度为 190 ℃，反应时间为 9 h；在上述的反应条件下反应，目标产物 SAPE 的收率高达 90.0%以。确定合成 SAPS 的较佳反应条件为：以 SO_3 为磺化剂对 SAPE 进行磺化，SO_3 浓度为 4 mol/L（1,2-二氯乙烷溶液），第一阶段反应时间为 2 h，第一阶段反应温度为 25 ℃，第二阶段反应时间为 2 h，第二阶段反应温度为 45 ℃，在上述的反应条件下反应，目标产物 SAPS 的收率可达 98.0%，磺化度可达 1.36。

（2）对双十二烷基二苯醚磺酸钠（DAPS）的合成工艺进行探索。首先在上述合成 SAPE 的研究基础上，通过正交实验确定合成双十二烷基二苯醚（DAPE）的较佳反应条件为：以 SAPE 和十二醇为原料，固酸为催化剂，单十二烷基二苯醚与十二醇的摩尔比为 1∶1，反应温度为 190 ℃，反应时间为 8 h。在上述的反应条件下反应，产物中双十二烷基二苯醚与单十二烷基二苯醚的摩尔比最大，

并且目标产物 DAPE 的收率较高，可达 73.3%；然后以合成 SAPS 的较佳工艺条件制备 DAPS，目标产物 DAPS 的收率可达 85.3%，磺化度可达 1.25。

（3）对所合成的系列 DDES 的溶解性能、乳化性能、抗硬水性能、热稳定性能、临界胶束浓度（CMC）及最小表面张力等性能进行测定，并与常用的表面活性剂十二烷基苯磺酸钠（SDBS）的性能进行对比，测试结果表明：所合成的系列 DDES 溶解性能优良，在酸、碱及极性的较低溶剂（如甲苯、乙醇等）中溶解性均较佳，其溶解性能明显优于 SDBS；所合成的部分 DDES 的乳化性能优于 SDBS，且其水溶液均为水包油型乳液；所合成的系列 DDES 的 CMC 值均远小于 SDBS 的 CMC 值，性能最佳的 DDES 的 CMC 值仅为 SDBS 的 10%；所合成的系列 DDES 的抗硬水能力明显优于 SDBS 的抗硬水能力，且其平均稳定性均为 5 级（最优级）；所合成的部分 DDES 热稳定性能优于 SDBS，热稳定性能最佳的 DDES 的热分解温度为 398 ℃。

（4）本论文设计了年产 1200 吨 SAPS 的工业化方案，在工艺流程确定、物料平衡图绘制、物料衡算、能量衡算以及主要设备的工艺计算等方面进行了深入的探讨，为工业化清洁生产 DDES 提供了可靠依据。通过成本核算，确定在本论文提出的工艺条件下，SAPS 的工艺成本为 17447 元/吨，利税超过 10000 元/吨。

关键词：十二烷基二苯醚磺酸钠 固体酸 清洁生产 性能测试 工业化方案

ABSTRACT

ADPEDS has many excellent performance as a kind of excellent versatility surfactant. In addition to being used as a special high performance detergent, it can also be used in many industrial fields, such as tertiary recovery, emulsion polymerization industry, printing and dyeing industry. The production of ADPEDS has been industrialized abroad, and the key production technology is monopolized by foreign companies. Research on this product was confined to the laboratory in domestic and its industrial production has not been reported, resulting in , its supply mainly rely on imports. So, research on this kind of surfactant is of great significance.

Firstly, production process of DDES was studied in this paper, and the best reaction conditions were determined by optimizing the synthesis process. Secondly, the performance of series of products synthesized in the paper were tested and analyzed. The specific research contents and results are as follows:

(1). SAPE was synthesized by diphenyl ether and lauryl alcohol under the action of solid acid. Series SAPS was obtained by sulfonation and neutralization of SAPE. Considering the influence of various factors on the reaction, the best reaction conditions for synthesis of SAPE are as follows: Mole ratio of diphenyl ether and lauryl alcohol is 4∶1, reaction temperature is 190 ℃, the reaction time was 9 h. In this best reaction conditions, the yield of SAPE could reach more than 90.0%. The best reaction conditions for synthesis of SAPS are as follows: SO_3 was sulfonating agent, the concentration of SO_3 was 4 mol/L, the first stage reaction time was 2 h, the first stage reaction temperature was 25 ℃, the second stage reaction time was 2 h, the second stage reaction temperature was 45 ℃. In this best reaction conditions, the yield of SAPS reached 98.0%, and the sulfonated degree reached 1.36.

(2). The synthesis process of DAPS was explored. On the basis of studying the synthesis of SAPE, the best reaction conditions for synthesis of DAPE by orthogonal experiment were choosed as: DAPE was synthesized by SAPE and lauryl alcohol under the action of solid acid, mole ratio of SAPE and lauryl alcohol was 1∶1, reaction

temperature was 190 ℃, the reaction time was 8 h, In the above reaction conditions, the yield of DAPE reached 73.3%. DAPS was synthesized under the best condition of preparing SAPS. The yield of DAPS reached 85.3%, and the sulfonated degree reaches 1.25.

(3). The performances of series DDES were tested and analyzed, such as solubility, emulsification, resistant to hard water, thermal stability, critical micelle concentration (CMC), the minimum surface tension, and then compared their performance with that of SDBS. The results showed that the solubility of DDES was very good, and it has good performance in acid, alkali and low polarity solvent. The solubility of DDES was obviously better than that of SDBS. The emulsification performance of part of DDES was better than SDBS, and its aqueous solution was oil-in-water emulsion. The CMC of series DDE were all far less than that SDBS, and the CMC of part of DDES was just 10% of SDBS.

(4). An industrialization plan of the produnction of SAPS about 1200 t/y SAPS was designded, and the process calculation, material balance diagram, calculation about material and energy, and main equipment determination were conducted in-depth discussion. The reliable basis for industrial cleaner production of DDES is provided. After economic accounting, the cost of SAPS production process is 17447 yuan / ton, and the profit and tax is more than 10000 yuan / ton.

Keywords: DDES, Solid acid, Cleaner production, Performance testing, Industrialization programs

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