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硕 士 学 位 论 文

超临界流体技术制备含香精香料的颗粒

Preparation of Flavor-Containing Particles by Supercritical Technologies

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摘 要

超临界流体技术作为一项绿色化学工艺技术，特别适用于食品用各种香精香料微胶囊或其复合颗粒的制备。本研究主要利用超临界流体负载技术制备包括薄荷醇和茶香为主的负载型香精香料复合颗粒，也涉及超临界流体技术制备高负载量的负载材料 SiO_2，以及建立的超临界流体萃取－负载耦合装置制备批量(公斤级)香精香料颗粒产品。

应用溶胶-凝胶法，以水玻璃为原料，制备湿凝胶，再采用超临界 CO_2（SC-CO_2）干燥制备出高负载量 SiO_2 负载材料。研究表明，SC-CO_2 干燥技术获取的 SiO_2 比常规护孔干燥技术操作更为方便，产品没有明显的聚积状态，且产品的孔容和平均孔径更大。

应用超临界负载技术，考察负载时间、负载温度和负载压力条件下，三种负载材料（SiO_2、活性炭和β-环糊精（β-CD））对薄荷醇香料的负载效果。研究表明，在所实验的条件下，SiO_2 对薄荷醇的负载量均高于其他两种材料，并且三种负载材料均有较优的负载条件：在考察范围内 SiO_2 和活性炭的较佳负载条件为 35.0℃、12.1MPa；β-CD 为 40.0℃，9.8MPa。采用低压氮气分别在 25.0℃和 40.0℃两种温度条件下对负载样品进行吹扫时，结果显示，SiO_2 具有较好的常温持香能力和控制释放效果，活性炭控制释放效果一般，而β-CD 的持香能力较差。

针对卷烟加香产品，制备大颗粒（40 ~ 60 目）SiO_2，建立并采用超临界萃取-负载一体化装置，制备薄荷醇/SiO_2、水/SiO_2 和茶香/SiO_2 三种负载型产品。研究表明，大颗粒 SiO_2 对薄荷醇的负载量有所降低。此外，采用 25.0℃、低压氮气对大颗粒的负载样品进行吹扫时，除了薄荷醇的保留率较高（达到 84.3%）

外，水和茶香的保留效果不佳；采用 40.0℃、低压氮气对大颗粒负载样品进行吹扫时，薄荷醇的保留率达到 66.2%以上，控释效果一般，而水和茶香的控制释放均匀，效果良好。

为解释、讨论薄荷醇负载条件对负载量的变化的影响，采用 PR 状态方程（Peng Robinson equation of state, PR EoS)计算了实验条件下的薄荷醇-CO_2的气液平衡数据。计算结果表明：当温度固定在 35.0℃，小于 12MPa 时，超临界相中薄荷醇浓度逐渐升高，并且增大趋势明显；大于 12MPa 时，超临界相中薄荷醇浓度变化趋缓；当压力固定在 9.8MPa 时，随温度升高，超临界相中薄荷醇浓度逐渐减小，并且减小趋势逐渐增大。计算结果可以较好地解释负载量随压力和温度的变化情况。

关键词：SiO_2；薄荷醇；超临界干燥；超临界萃取-负载耦合；气液平衡

Abstract

As a green chemistry technology, supercritical fluid techniques are particularly applicable in preparation of various flavor or fragrance -containing particles (microencapsules or composite particles) for uses in food industry. In this study, the supercritical fluid loading technology was used to prepare menthol and tea flavors loading particles. In addition, supercritical fluid drying was applied to preparation of the loading material SiO_2, and a coupled supercritical fluid extraction –supercritical loading apparatus was set up for production of kilogram-grade flavor or fragrance -containing particles.

Water glass was used as the silica precursor to prepare wet gel by the sol-gel method, which was further dried by using supercritical CO_2 to obtain the loading material SiO_2. Results show that the SiO_2 dried by supercritical CO_2 is more dispersed than that dried by conventional drying with pore protectant. Although the SiO_2 particles from the two methods have nearly the same specific surface area, the one from supercritical CO_2 has relatively large pore volume and average pore size.

The loading amounts of menthol in three loading materials, namely SiO_2, activated carbon and β-cyclodextrin were systematically evaluated under various conditions (the loading time, loading temperature and pressure) by supercritical CO_2 loading technology. Results show that the loading of menthol on SiO_2 is the highest under all the investigated conditions; all the three loading materials show optimal loading conditions in the range of 8.0 ~14.0MPa and 30.0 ~ 45.0℃: the optimal loading conditions for SiO_2 and activated carbon are 35.0℃ and 12.1MPa, and 40.0 ℃ and 9.8MPa for β-cyclodextrin. By purging low pressure nitrogen through the menthol-containg samples at 25.0℃ and 40.0℃, respectively, results reveal that the SiO_2 has the best retention of menthol at 25.0℃ with control release, and the activated carbon also has good control release. On the contrary, β-cyclodextrin shows a rapid release.

With respect to the use as the cigratte flavor product, large particles of SiO_2 (40 ~ 60 mesh) were prepared by using the superciritcal fluid drying approach, which are then employed to produce menthol/SiO_2, water/SiO_2 and tea flavor/SiO_2 particles with a supercritical fluid extraction － supercritical loading coupling apparatus. Results find that the menthol loading decreases in these large size particles, compared to the previous fine SiO_2 particles. When purged through low pressure nitrogen at 25.0℃, only menthol/SiO_2 shows good retention ratio (up to 84.3%). When urged at 40.0℃, the menthol/SiO_2 still shows relatively high retention (more than 66.2%), while water/SiO_2 and tea flavor/SiO_2 show excellent control release, which can be potentially used as the cigratte flavor products.

The Peng Robinson equation of state was applied to the calculation of vapor-liquid phase equilibrium data of the menthol-CO_2 system in order to explain the effect of loading conditions on the loading of menthol. Results show that when the pressure is less than 12 MPa, the calculated concentration of menthol in CO_2 at 35℃ increases significantly, while it is higher than 12MPa, the concentration is almost unchanged. As the temperature increases, the calculated concentration of menthol in CO_2 at 9.8 MPa decreases obviously. These calculations support the special changes of the loading of menthol following the loading pressure and temperature.

Key words: SiO_2, menthol, supercritical drying, coupled supercritical extraction-loading, vapor-liquid equilibrium

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