

学校编码：10384

分类号：_____ 密级：_____

学号：20620091151279

UDC_____

廈門大學

碩 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

朱林静

指导教师姓名：李军 教授

专业名称：化学工程

论文提交日期：2012年06月

论文答辩时间：2012年06月

学位授予日期：2012年 月

答辩委员会主席：__

评阅人：__

2012年06月

厦门大学博硕士学位论文摘要库

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果,均在文中以适当方式明确标明,并符合法律规范和《厦门大学研究生学术活动规范(试行)》。

另外,该学位论文为()课题(组)的研究成果,获得()课题(组)经费或实验室的资助,在()实验室完成。(请在以上括号内填写课题或课题组负责人或实验室名称,未有此项声明内容的,可以不作特别声明。)

声明人(签名):

年 月 日

厦门大学博硕士学位论文摘要库

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

() 1. 经厦门大学保密委员会审查核定的保密学位论文，
于 年 月 日解密，解密后适用上述授权。

() 2. 不保密，适用上述授权。

(请在以上相应括号内打“ ”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。)

声明人（签名）：

年 月 日

厦门大学博硕士学位论文摘要库

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($\beta\text{-CD}$))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; $\beta\text{-CD}$ 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 $\beta\text{-CD}$ 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-CO₂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: SiO₂; 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 SiO₂, 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 CO₂ to obtain the loading material SiO₂. Results show that the SiO₂ dried by supercritical CO₂ is more dispersed than that dried by conventional drying with pore protectant. Although the SiO₂ particles from the two methods have nearly the same specific surface area, the one from supercritical CO₂ has relatively large pore volume and average pore size.

The loading amounts of menthol in three loading materials, namely SiO₂, activated carbon and β-cyclodextrin were systematically evaluated under various conditions (the loading time, loading temperature and pressure) by supercritical CO₂ loading technology. Results show that the loading of menthol on SiO₂ 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 SiO₂ 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-containing samples at 25.0 and 40.0 , respectively, results reveal that the SiO₂ 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 cigarette flavor product, large particles of SiO₂ (40 ~ 60 mesh) were prepared by using the supercritical fluid drying approach, which are then employed to produce menthol/SiO₂, water/SiO₂ and tea flavor/SiO₂ 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 SiO₂ particles. When purged through low pressure nitrogen at 25.0 MPa, only menthol/SiO₂ shows good retention ratio (up to 84.3%). When urged at 40.0 MPa, the menthol/SiO₂ still shows relatively high retention (more than 66.2%), while water/SiO₂ and tea flavor/SiO₂ show excellent control release, which can be potentially used as the cigarette flavor products.

The Peng Robinson equation of state was applied to the calculation of vapor-liquid phase equilibrium data of the menthol-CO₂ 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 CO₂ at 35 °C increases significantly, while it is higher than 12MPa, the concentration is almost unchanged. As the temperature increases, the calculated concentration of menthol in CO₂ 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: SiO₂, menthol, supercritical drying, coupled supercritical extraction-loading, vapor-liquid equilibrium

目 录

第一章 文献综述	1
1.1 前言	1
1.2 香精香料微胶囊及壁材	2
1.2.1 制备香精香料微胶囊的主要方法	2
1.2.2 壁材简介	3
1.3 超临界流体及相关技术	4
1.3.1 超临界流体简介	4
1.3.2 超临界流体技术	6
1.4 本文的立意和研究内容	12
第二章 SiO₂ 的制备和超临界干燥	13
2.1 引言	13
2.2 实验部分	14
2.2.1 实验材料	14
2.2.2 实验装置及流程	14
2.2.3 分析方法	16
2.3 结果与讨论	16
2.3.1 SEM 扫描电镜分析	16
2.3.2 XRD 的物相分析	18
2.3.3 IR 结构分析	18
2.3.4 BET 数据分析	19
2.4 小结	20
第三章 超临界负载技术制备薄荷醇颗粒香料	21
3.1 引言	21
3.2 实验部分	21
3.2.1 实验材料	21
3.2.2 实验装置及流程	22
3.2.3 分析方法	25
3.3 实验结果及讨论	26

3.3.1 饱和负载时间的测定	26
3.3.2 不饱和负载曲线	27
3.3.3 超临界负载与常压负载的对比	28
3.3.4 温度的影响	29
3.3.5 压力的影响	30
3.3.6 N ₂ 吹扫测定保留率	31
3.3.7 超临界负载机理	33
2.4 小结	34
第四章 香精香料复合颗粒的中试放大	36
4.1 引言	36
4.2 实验背景	36
4.3 实验部分	37
4.3.1 实验材料	37
4.3.2 实验装置及流程	38
4.3.3 分析方法	40
4.3 实验结果和讨论	40
4.3.1 三种负载产品负载量的测定	40
4.3.2 N ₂ 吹扫实验	41
4.4 小结	43
第五章 薄荷醇-CO₂气液平衡研究	44
5.1 引言	44
5.2 薄荷醇-CO ₂ 气液平衡模型	44
5.3 模型计算结果和讨论	46
5.4 小结	49
第六章 结论	51
参 考 文 献	53
致 谢	62

Table of Contents

Chapter 1 Introduction	1
1.1 Preface	1
1.2 Flavor microcapsules and wall materials	2
1.2.1 Papperation methods of flavor microcapsules	2
1.2.2 Brief introduction of wall materials	3
1.3 Supercritical fluid technology	4
1.3.1 Introduction of supercritical fluid	4
1.3.2 Introduction of supercritical fluid technologies	6
1.4 Research objectives and contents	12
Chapter 2 Papperation and supercritical drying of SiO₂	13
2.1 Introduction	13
2.2 Experimental	14
2.2.1 Materials	14
2.2.2 Apparatus and procedure	14
2.2.3 Analytical methods	16
2.3 Results and discussion	16
2.3.1 SEM analysis	16
2.3.2 XRD analysis	18
2.3.3 IR analysis	18
2.3.4 BET analysis	19
2.4 Conclusion	20
Chapter 3 Papperation of menthol loading particles by supercritical loading technology	21
3.1 Introduction	21
3.2 Experimental	21
3.2.1 Materials	21

3.2.2	Apparatus and procedure-----	22
3.2.3	Analytical methods -----	25
3.3	Results and discussions-----	26
3.3.1	Measurement of supercritical saturated loading time -----	26
3.3.2	Unsaturated loading curve -----	27
3.3.3	Comparison of supercritical loading and atmospheric loading -----	28
3.3.4	Influence of temperature -----	29
3.3.5	Influence of pressure -----	30
3.3.6	Measurement of retention ratios by N ₂ -blowing method -----	31
3.3.7	The mechanism of supercritical loading process -----	33
2.4	Conclusions -----	34
Chapter 4 Pilot productions for flavor-loading particles-----		36
4.1	Introduction -----	36
4.2	Background -----	36
4.3	Experimental -----	37
4.3.1	Materials -----	37
4.3.2	Apparatus and procedure-----	38
4.3.3	Analytical methods -----	40
4.3	Results and discussion-----	40
4.3.1	Measurement of loading ratios of three loading products -----	40
4.3.2	Measurement of retention ratios by N ₂ -blowing method-----	41
4.4	Conclusions -----	43
Chapter 5 Vapor-liquid equilibrium of menthol-CO₂ system -----		44
5.1	Introduction -----	44
5.2	Vapor-liquid equilibrium model of menthol-CO₂ system-----	44
5.3	Results and discussions of model calculation -----	46
5.4	Conclusions -----	49
Chapter 6 Summary -----		51
References-----		53

Acknowledgement----- 62

厦门大学博硕士学位论文摘要库

厦门大学博硕士学位论文摘要库

Degree papers are in the "[Xiamen University Electronic Theses and Dissertations Database](#)". Full texts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to etd@xmu.edu.cn for delivery details.

厦门大学博硕士论文摘要库