

Chemical/Biochemical Technology and Biomaterial Energy Resource

— Proceedings of The 3rd National Chemical and Biochemical Engineering Annual Meeting

— Proceedings of The 1st Academic Forum of Guangxi Chemistry & Chemical Engineering Graduate Student

化工/生化技术与生物质能源



- 第三届全国化学工程与生物化工年会论文选编
- 首届广西化学化工研究生学术论坛论文选编

童张法 主编



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· 北 京 ·

本书在全国化学工程与生物化工年会执行委员会的领导下,由第三届年会组委会和首届广西化学化工研究生学术论坛学术委员会推荐的编委会具体负责编写,并得到了各论文作者的大力支持,共选编了第三届全国化学工程与生物化工年会论文 98 篇、首届广西化学化工研究生学术论坛论文 24 篇。这些论文涵盖了化学工程/生物化工科学技术及其在生物质能源应用开发领域的各个方面,既有关于化工科学及理论最新研究成果,又有大量结合化学工程与技术实践背景的应用研究成果与实用化工技术创新;既包括了我国化工过程研究中的新理论、新技术和新手段,也展现了与之紧密相关的材料、生物、生命、制药、能源、电子信息等交叉领域的科研进展,集中反映了我国化学工程与技术学科学术研究的前沿动态和最新成果。本书对高等院校、科研院所的化学工程与技术、生物工程与技术类相关教师、科研人员、研究生以及在校大学生进行科研工作或参与课题开发等均有很好的参考和借鉴价值。

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前 言 一

化学工程作为工程技术学科之一，直接服务于对国民经济有着重大影响和对国家命运具有决定作用的化工行业。随着新能源、新材料、生物技术等新兴产业的出现，在过去 100 年的发展基础上孵化出材料化学工程、生物化学工程、能源化学工程、资源化学工程、环境化学工程等新的学科分支和发展空间。因此，为适应学科的新发展，促进学科交叉和融合，在中国化工学会的大力支持下，其所属的“化学工程专业委员会”和“生物化工专业委员会”根据国内外学科及产业发展的需要，应广大化学工程与生物化工工作者的强烈要求，决定从 2004 年起召开首届全国化学工程与生物化工年会（NCBE），以此促进我国化学工程与生物化工科学技术的交流与发展，展示该领域的研究现状和水平，鼓励创新性和前沿性的学术思想和理论。

在全国化学工程与生物化工年会执行委员会的有力领导下，至今已经成功举办了两届 NCBE 年会。在南京工业大学和北京化工大学举办的第一届和第二届会议上，不仅有十多位院士及国外知名学者出席并作大会报告，国内近百所高校及科研院所、国家有关部门、部分国外企业、国内企业等也派出 800 多名代表参加，会议规模大、层次高，已经成为化工界的学术盛会，产生了广泛的社会影响。2006 年中国 NCBE 年会将于 11 月 11 日在南宁隆重开幕。此次年会将为期四天，由中国化工学会化学工程专业委员会与生物化工专业委员会主办，广西大学与广西科学院承办，中国科学院、中国工程院多位院士和教育部多位长江学者、国家杰出青年基金获得者、国外著名专家学者出席本次大会。

第三届全国化学工程与生物化工年会的主题是《化工/生化技术与生物质能源》。生物质能源是全球继煤炭、石油和天然气化石能源之后的第四大能源。生物质能源的数量丰富并且是环境友好型能源，从资源潜力、生产成本以及可能发挥的作用分析，包括生物燃油产业化在内的生物质能源产业化开发技术将成为维护中国能源安全的重要发展方向。年会的主要目的是交流在化工/生化科学与技术各个分支领域的最新研究成果，讨论它们的现代论题和方法；特别强调与推动面向经济、社会可持续发展，与相关学科交叉的化工科学与技术研究。年会组委会共收到会议论文 1000 余篇，录用 980 篇。根据部分论文作者希望正式出版论文的要求，征得年会执委会的同意，通过年会组委会推荐的专家评审，选编了 98 篇年会论文由化学工业出版社结集出版。

全书由童张法、刘幽燕统稿，刘雄民、陈小鹏、冯庆革、崔学明、韦藤幼、韦宇拓、庞浩、李飘英、文衍宣、刘琨，林翠梧、黎铨海、唐艳葵等编委参与了审稿工作，广西大学李立硕、邹昀等参与了具体的打印、修改、编辑工作。论文集的出版还得到了广西大学重点学科建设经费和广西教育厅学位点建设经费的资助。

由于编者水平有限，时间仓促，书中难免存在不足与疏漏之处，敬请各位论文作者与读者谅解，并提出宝贵意见。



2006 年 10 月 23

前 言 二

一个民族、一个国家的兴旺与教育的发展是息息相关的,教育要为经济和社会发展服务。创新是知识经济时代的灵魂,而创新归根结底是教育的竞争,人才的竞争,特别是高层次人才竞争,因此创新教育也成为适应时代发展、迎合知识经济社会需要而兴起的一种新的教育理念。作为最高层次的高等教育,研究生教育肩负着为社会培养高素质、高层次创造性人才的重任,实施研究生的创新教育关键在于教育观念的改革和新型培养模式的建立。近年来,教育部在研究生教育领域着力推进“研究生教育创新计划”,其目的就是要深入探索新形势下研究生教育规律,更新观念,深化改革,推进创新,建立起与社会主义市场经济体制相适应的研究生教育体制和运行机制;加强研究生培养基地建设,改善培养条件,促进优质资源共享,从而为研究生创新教育营造一个激发式的环境和立体的支撑。

广西壮族自治区位于祖国南疆边陲、沿海沿江沿边,西部大开发、中国-东盟自由贸易区的建立等都为加快地区经济社会发展、改善地区落后现状、实现富民兴桂新跨越战略提供了千载难逢的机遇,具有创新思维和意识的高层次人才对广西未来发展尤其显得重要和迫切。为加强广西研究生教育创新工作,2006年自治区学位委员会、教育厅开始实施2006~2010年广西研究生教育创新计划,从而有计划、有步骤地全面提升自治区研究生教育质量,增强自治区研究生教育的实力,更好地为地区经济建设、科技进步和社会发展服务。

举办研究生学术论坛是研究生创新计划的重要组成部分。在研究生创新计划的资助下,借助2006年第三届全国化学工程与生物化工年会在南宁召开的难得机遇,广西大学研究生会联合化学化工学院研究生分会于2006年11月13日举办首届广西化学化工研究生学术论坛,论坛主题为“绿色化学、生态化工”。此次论坛收到许多高质量论文,论文内容涉及面广,在化学工艺、生物化工、无机化学、有机化学、分析化学、物理化学、材料化学、环境保护、天然产物开发、精细化工等领域都有相关研究和论文报道。不少研究都与广西地方经济结合紧密,而且很多论文都是研究生参与导师承担的国家自然科学基金、自治区三项基金、教育厅科研基金等项目研究所取得的科研成果,也有部分论文是在广西研究生科研创新项目资助下完成的。论文充分展现了目前广西化学化工类研究生的学术水平和成果,也折射出研究生较强的创新意识和创新能力。

纵观本次论坛,有很多经验值得总结,也有很多成果值得推广。由董张法教授主编的“首届广西化学化工研究生学术论坛论文选编”主要收录了论坛中部分优秀论文,它直接反映了广西高校化学化工类研究生的科研水平和成果,体现了自治区各高校在研究生创新意识和能力培养方面的理念和思路。我相信此书对自治区化学化工类研究生和指导教师很有裨益,并对自治区创新教育事业的发展、化学化工类学科学位点建设起到促进作用。



2006年10月23

第三届全国化学工程与生物化工 年会论文选编

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The study on the phase equilibria of the CO₂-H₂O and CO₂-H₂O-NaCl systems

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Abstract: CO₂ geological sequestration is becoming a hot issue. In order to study the feasibility evaluation of CO₂ geological sequestration, it is needed to understand the complicated multiple-phase equilibrium of aqueous solutions with CO₂ and multi-ions under geological conditions of a wide temperature and pressure range, which are also essential for designing separation equipments in chemical or oil-related industries. For this purpose, three different models (the electrolyte NRTL [5-8] (ELECNRTL), the electrolyte NRTL combining with Helgeson model [11] (ENRTL-HG), Pitzer activity coefficient model [12-14] combining with Helgeson model [11] (PITZ-HG)) have been used to calculate the Vapor-Liquid phase equilibrium of CO₂-H₂O and CO₂-H₂O-NaCl systems. For CO₂-H₂O system, the calculation results agree with the experimental data very well at low and medium pressures (0~20MPa), but there are great discrepancies above 20MPa. For the calculated water content data at 473.15K, the calculated results agree with the experimental data quite well. For CO₂-H₂O-NaCl system, PITZ-HG model show better results than ELECNRTL and ENRTL-HG models at the NaCl concentration of 0.52m. But for the NaCl concentration of 3.997m, using ELECNRTL and ENRTL-HG models we can get better results than using PITZ-HG model. This paper proves that the thermodynamic calculations can satisfy the needs of the calculation of the sequestration capacity for the temperature and pressure range of disposal of CO₂ in deep saline aquifers. But considering the injection of carbon dioxide into depleted hydrocarbon reservoirs, more accurate thermodynamic calculations are needed at high temperatures and pressures (above 398.15K and 31.5MPa).

Key words: CO₂-H₂O, CO₂-H₂O-NaCl, high temperature high pressure, phase equilibrium

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1 INTRODUCTION

The increase of the concentration of CO₂ leads to a significant climate warming and weather changes. In 1997, the Kyoto Protocol clearly states the reduction of greenhouse gases emissions^[1]. Since CO₂ is believed that environmental consequences of such an approach would be broadly neutral^[4].

In order to predict the sequestration potential and to study the long-term behavior of carbon dioxide in the geologic reservoirs, it is needed to study the complicated multiple-phase equilibrium of the aqueous solution containing CO₂ and ions (Na⁺, K⁺, Mg²⁺, Ca²⁺ and Cl⁻ etc.) under the geological conditions of a wide temperature and pressure range. Since the phase behavior of the CO₂-H₂O-ions responsible for about 64% of the enhanced "greenhouse effect"^[2], the disposal of CO₂ has become concerned world widely. Geological sequestration

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is currently attracting attention^[3]. Its system is complicated, and Na^+ and Cl^- are the main components, it is usually simplified to study the phase equilibrium for the $\text{CO}_2\text{-H}_2\text{O}$ and $\text{CO}_2\text{-H}_2\text{O-NaCl}$ systems. For this purpose, three different models have been used to calculate the Vapor-Liquid phase equilibrium of $\text{CO}_2\text{-H}_2\text{O}$ and $\text{CO}_2\text{-H}_2\text{O-NaCl}$ systems and the calculation results are compared with the experimental data.

2 CALCULATIONS WITH SELECTED THERMODYNAMIC MODELS

In this paper, three different models have been used to calculate the Vapor-Liquid phase equilibrium of $\text{CO}_2\text{-H}_2\text{O}$ and $\text{CO}_2\text{-H}_2\text{O-NaCl}$ systems. And the calculation results are compared with the experimental data in order to evaluate the experimental data further more.

In the first thermodynamic model, the electrolyte NRTL (ELECNRTL) activity coefficient model^[5-8] is used to calculate the activity coefficient of the aqueous solution, the Redlich-Kwong equation of state^[9] is used to calculate the fugacity coefficient for the vapor phase. The pair parameters of the ELECNRTL model are obtained by regressing vapor pressure and mole fraction data at 100°C ^[10]. The second model (ENRTL-HG) is similar to the ELECNRTL method, except it uses the Helgeson model for standard properties calculations. Here we use SUPCRT92^[11] to calculate the standard properties. In the third model (PITZ-HG), Pitzer activity coefficient model^[12-14] is used to calculate the activity coefficient of the aqueous solution, the parameters for the Pitzer model are available from Pitzer's series^[12-14] on the thermodynamics of electrolytes. SUPCRT92^[11] is used for standard properties calculations, and the Redlich-Kwong-Soave equation of state^[15-17] is used to calculate the vapor phase fugacity coefficient. In all the three methods, the solubility of CO_2 is modeled using Henry's law.

2.1 $\text{CO}_2\text{-H}_2\text{O}$ system

In this work, the phase equilibrium of $\text{CO}_2\text{-H}_2\text{O}$ system under three temperatures (323.15, 373.15, 473.15K) is firstly calculated by the three different models. The pressure conditions studied is from 0 to 80MPa, and the results are shown in Figure 1.

As is shown in Figure 1, for the calculated CO_2 solubility in H_2O -rich phase under the temperatures of 323.15, 373.15 and 473.15K, the calculated CO_2 solubility under the pressures below 10MPa agrees with the experimental data quite well. However, when the pressure is above 10MPa, there are great discrepancies. And the discrepancies are more obvious as the temperature increases. Although the calculated results didn't agree with the experimental data very well at high pressures, the temperature and pressure dependence of the CO_2 solubilities is consistent with the experimental data. From the comparison of our calculated results with the experimental data, we can see the three models can't describe the CO_2 solubility of high pressures very well.

For the calculated water content in CO_2 -rich phase at 323.15K, the results below 10MPa agrees with the experimental data very well, but there are great discrepancies above 10MPa. The results at 373.15K show that calculated water content data below 20MPa are consistent with the experimental data. And the agreements of the results at 373.15K are much better than that at 323.15K. Considering the calculation results at 473.15K, the calculated water content data agree with the experimental data quite well, much better than that at the other two temperatures.

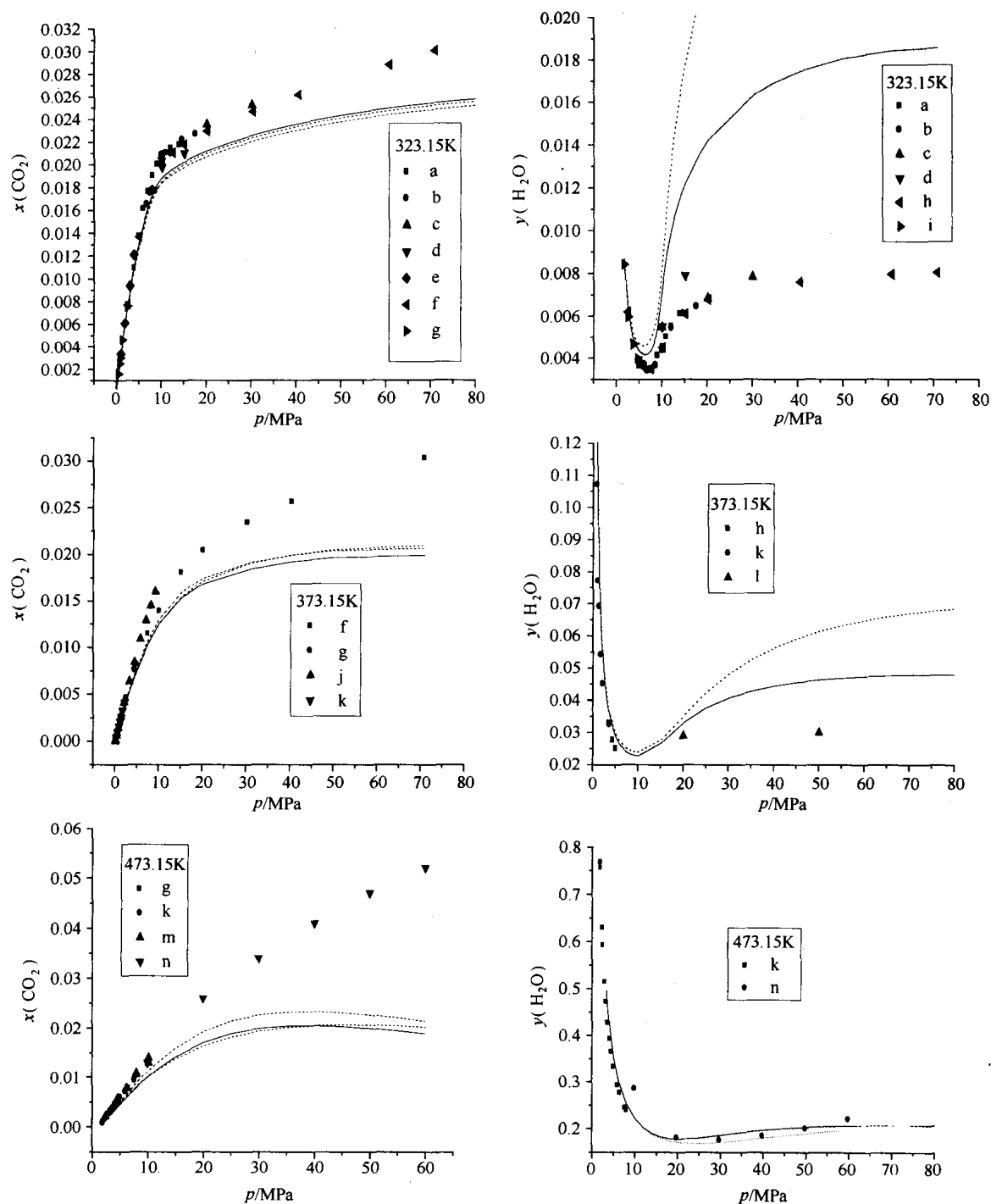


Figure. 1 Mole fractions of CO₂ in H₂O-rich phase and mole fractions of H₂O in CO₂-rich phase for CO₂-H₂O system at 323.15, 373.15 and 473.15K. Experimental data: a. Bamberger et al. [18], b. Briones et al. [19], c. Dohrn et al. [20], d. D'Souza et al. [21], e. Matous et al. [22], f. Wiebe and Gaddy [23], g. Zawisza and Malesinska [24], h. Wiebe and Gaddy [25], i. Coan and King [26], j. Kiepe et al. [27], k. Müller et al. [28], l. Töedheide and Franck [29], m. Nighswander et al. [30], n. Takenouchi et al. [31]. Calculated: —, ELECNRTL, ..., ENRTL-HG, ..., PITZ-HG.

2.2 CO₂-H₂O-NaCl system

We also calculated the phase equilibria of CO₂-H₂O-NaCl system under the temperature of 313.15 and 333.15K. The concentrations of the NaCl are 0.52m and 3.997m. Also the pressures are up to 80MPa. The comparison of the calculated results with the experimental data is shown in Figure 2.

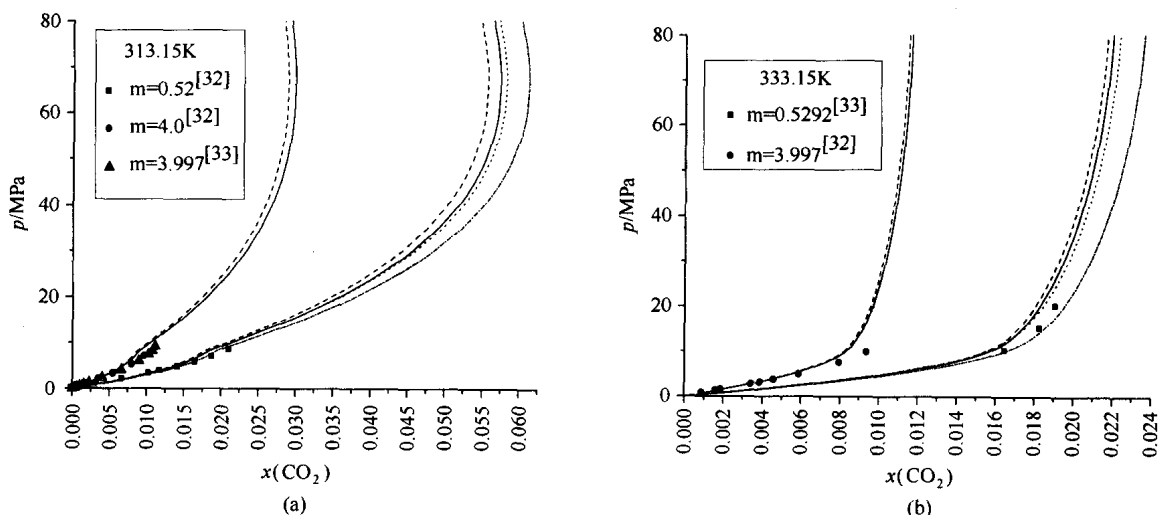


Figure. 2 Mole fractions of CO₂ in H₂O-rich phase for CO₂-H₂O-NaCl system at 313.15 and 333.15K. Calculated: (a) —, ELECNRTL (m=0.52, 3.997), ---, ENRTL-HG (m=0.52, 3.997), - · - · - ·, PITZ-HG (m=0.52), ... , PITZ-HG (m=3.997); (b) —, ELECNRTL (m=0.5292, 3.997), ---, ENRTL-HG (m=0.5292, 3.997), - · - · - ·, PITZ-HG (m=0.5292), ... , PITZ-HG (m=3.997) .

From Figure 2 it is found that for the NaCl concentration of 0.52m, the calculated results by the three different models agree well with the experiment data. And the PITZ-HG model brings the best agreement. For the NaCl concentration of 3.997m, the calculated results by ELECNRTL and ENRTL-HG models show good agreements with the experimental data. But there are great discrepancies between the calculation results and the experimental data when using PITZ-HG model, which also shows that the PITZ-HG model should be modified when using in high salt concentrations. In general, the three models not only well describe the pressure effect and temperature effect on the CO₂ solubility, but also the salting-out effect. At constant pressure, the solubility of CO₂ in the aqueous solution decreases with increasing salt concentrations.

From the calculations with selected three thermodynamic models, we can find that the existing thermodynamic models can nearly satisfy the needs of the calculations for the sequestration capacity in the temperature and pressure range for disposal of CO₂ in deep saline aquifers. But for the temperature and pressure as high as 398.15K and 31.5MPa, which may reach in the abandoned oil and gas reservoirs, the models can't obtain very accurate results.

3 CONCLUSIONS

The phase equilibria of the CO₂-H₂O and CO₂-H₂O-NaCl systems in a wide temperature and pressure range are calculated with three selected models. The following conclusions are drawn:

(1) For CO₂-H₂O system, our calculated mutual solubilities of CO₂ and H₂O showed that the agreements between the calculation results and the experimental data are very good at low and medium pressures (0~20MPa). When the pressure is above 20MPa, there are great discrepancies. But for the calculated water content data at 473.15K, the calculated results agree with the experimental data quite well. For CO₂-H₂O-NaCl system, PITZ-HG model shows better results than ELECNRTL and ENRTL-HG models at the NaCl concentration of 0.52m. But for the NaCl concentration of 3.997m, using ELECNRTL and ENRTL-HG models we can get better results than using PITZ-HG model.

(2) From the results of the existing thermodynamic calculations, we can see that the models can satisfy the needs of the calculations for the sequestration capacity in the temperature and pressure range for disposal of CO₂ in deep saline aquifers. But considering the injection of carbon dioxide into depleted hydrocarbon reservoirs, more accurate thermodynamic calculations are needed at high temperatures and pressures (more than 398.15K and 31.5MPa).

References

- [1] Ji, Y. H., Feng, X., Lu, X. H., "Analysis of economics and chemical engineering in the geological sequestration of carbon dioxide", *Chem. Ind. Eng. Progress, (in Chinese)* **25** (2), 171-175 (2006)
- [2] Bachu, S., "Sequestration of CO₂ in geological media: criteria and approach for site selection in response to climate change", *Energy Convers Manage*, **41**, 953-970 (2000)
- [3] Nicolas, S., Karsten, P., Jonathan, E. K., "CO₂-H₂O mixtures in the geological sequestration of CO₂. I. Assessment and calculation of mutual solubilities from 12 to 100°C and up to 600 bar", *Geochim Cosmochim Acta*, **67** (16), 3015-3031 (2003)
- [4] Grimston, M. C., Karakoussis, V., Fouquet, R., van der Vorst, R., Pearson, P., Leach, M., "The European and global potential of carbon dioxide sequestration in tackling climate change", *Climate Policy*, **1**, 155-171 (2001)
- [5] Renon, H., Prausnitz, J. M., "Local compositions in thermodynamic excess functions for liquid mixtures", *AIChE J.*, **14** (1), 135-144 (1968)
- [6] Chen, C. C., Britt, H. I., Boston, J. F., Evans, L. B., "Local Compositions Model for Excess Gibbs Energy of Electrolyte Systems: Part I: Single Solvent, Single Completely Dissociated Electrolyte Systems", *AIChE J.*, **28** (4), 588-596 (1982)
- [7] Chen, C. C., Evans, L. B., "A Local Composition Model for the Excess Gibbs Energy of Aqueous Electrolyte Systems", *AIChE J.*, **32** (3), 444-459 (1986)
- [8] Mock, B., Evans, L. B., and C.-C. Chen, "Thermodynamic Representation of Phase Equilibria of Mixed-Solvent Electrolyte Systems", *AIChE J.*, **32** (10), 1655-1664 (1986)
- [9] Redlich, O., Kwong, J. N. S., "On the Thermodynamics of Solutions V. An Equation-of-state. Fugacities of Gaseous Solutions", *Chem. Rev.*, **44**, 223-244 (1979)
- [10] Lide, D. R., CRC Handbook of Chemistry and Physics, 83th Edition, CRC Press, Boca Raton, Florida (2002)
- [11] Johnson, J. W., Oelkers, E., Helgeson, H. C., SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species and reactions from 1 to 5000 bar and 0 to 1000°C. *Comput. Geosci.*, **18**, 899-947 (1992)
- [12] Pitzer, K. S., Activity Coefficients in Electrolyte Solution, 2nd Edition, Chapter 3, CRC Press, Boston (1991)
- [13] Silvester, L. F., Pitzer, K. S., "Thermodynamics of Electrolytes. 8. High-Temperature Properties, Including Enthalpy and Heat Capacity, with Application to Sodium Chloride", *J. Phys. Chem.*, **81** (19), 1822-1828 (1977)
- [14] Chen, C. C., Britt, H. I., Boston, J. F., Evans, L. B., "Extension and Application of the Pitzer Equation for Vapor-Liquid Equilibrium of Aqueous Electrolyte Systems with Molecular Solutes", *AIChE J.*, **25**, 820-831 (1979)
- [15] Soave, G., "Equilibrium Constants for Modified Redlich-Kwong Equation-of-state", *Chem. Eng. Sci.*, **27**, 1196-1203 (1972)
- [16] Peneloux, A., Rauzy, E., Freze, R., "A Consistent Correction For Redlich-Kwong-Soave Volumes", *Fluid Phase Equilib.*, **8**, 7-23 (1982)
- [17] Kabadi, V., Danner, R. P., "A Modified Soave-Redlich-Kwong Equation of State for Water-Hydrocarbon Phase Equilibria", *Ind. Eng. Chem. Process Des. Dev.*, **24** (3), 537-541 (1985)

- [18] Bamberger, A. , Sieder, G. , Maurer, G. , "High-pressure (vapor + liquid) equilibrium in binary mixtures of (carbon dioxide + water or acetic acid) at temperatures from 313 to 353 K", *J. Supercrit. Fluids*, **17**, 97-110 (2000)
- [19] Briones, J. A. , Mullins, J. C. , Thies, M. C. , Kim, B. U. , "Ternary phase equilibria for acetic acid-water mixtures with supercritical carbon dioxide", *Fluid Phase Equilib.* , **36**, 235-246 (1987)
- [20] Dohrn, R. , Büenz, A. P. , Devlieghere, F. , Thelen, D. , "Experimental measurements of phase equilibria for ternary and quaternary systems of glucose, water, CO₂ and ethanol with a novel apparatus", *Fluid Phase Equilib.* , **83**, 149-158 (1993)
- [21] D'Souza, R. , Patrick, J. R. , Teja, A. S. , "High pressure phase equilibria in the carbon dioxide-n-hexadecane and carbon dioxide-water systems", *Can. J. Chem. Eng.* , **66**, 319-323 (1988)
- [22] Matous, J. , Sobr, J. , Novak, J. P. , Pick, J. , "Solubilities of carbon dioxide in water at pressure up to 40 atm", *Collect. Czech. Chem. Commun.* , **34**, 3982-3985 (1969)
- [23] Wiebe, R. , Gaddy, V. L. , "The solubility in water of carbon dioxide at 50, 75, and 100°C, at pressures to 700 atmospheres", *J. Am. Chem. Soc.* , **61**, 315-318 (1939)
- [24] Zawisza, A. , Malesinska, B. , "Solubility of carbon dioxide in liquid water and of water in gaseous carbon dioxide in the range 0.2-5 MPa and at temperatures up to 473 K", *J. Chem. Eng. Data* , **26**, 388-391 (1981)
- [25] Wiebe, R. , Gaddy, V. L. , "Vapor phase composition of carbon dioxide-water mixtures at various temperatures and at pressures to 700 atmospheres", *J. Am. Chem. Soc.* , **63**, 475-477 (1941)
- [26] Coan, C. R. , King, A. D. Jr. , "Solubility of water in compressed carbon dioxide, nitrous oxide, and ethane. Evidence for hydration of carbon dioxide and nitrous oxide in the gas phase", *J. Am. Chem. Soc.* **93**, 1857-1862 (1971)
- [27] Kiepe, J. Horstmann, S. , Fischer, K. , Gmehling, J. , "Experimental determination and prediction of gas solubility data for CO₂ + H₂O mixtures containing NaCl or KCl at temperatures between 313 and 393 K and Pressures up to 10 MPa", *Ind. Eng. Chem. Res.* , **41**, 4393-4398 (2002)
- [28] Müller, G. , Bender, E. , Maurer, G. , "Das Dampf-Flüssigkeits-gleichgewicht des Ternären Systems Ammoniak-Kohlendioxid-Wasser bei Hohen Wassergehalten im Bereich Zwischen 373 und 473 Kelvin", *Ber. Bunsen-Ges. Phys. Chem.* , **92**, 148-160 (1988)
- [29] Töedheide, K. , Frank, E. U. , "Das Zweiphasengebiet und die kritische Kurve im System Kohlendioxid-Wasser bis zu Drucken von 3500 bar", *Z. Phys. Chemie. Neue Folge.* , **37**, 387-401 (1963)
- [30] Nighswander, J. A. , Kalogerakis, N. , Mehrotra, A. K. , "Solubilities of carbon dioxide in water and 1 wt% NaCl solution at pressures up to 10 MPa and temperatures from 80 to 200 °C", *J. Chem. Eng. Data* , **34**, 355-360 (1989)
- [31] Takenouchi, S. , Kennedy, G. C. , "The binary system H₂O-CO₂ at high temperatures and pressures", *Am. J. Sci.* **262**, 1055-1074 (1964)
- [32] Jackson, K. , Bowman, L. E. , Fulton, J. L. , "Water solubility measurements in supercritical fluids and high-pressure liquids using near-infrared spectroscopy", *Anal. Chem.* , **67**, 2368-2372 (1995)
- [33] Rumpf, B. , Nicolaisen, H. , Ocal, C. , Maurer, G. , "Solubility of carbon dioxide in aqueous solutions of sodium chloride: experimental results and correlation", *J. Solution Chem.* , **23** (3), 431-448 (1994)

棕榈油脱臭馏出物制备生物柴油的研究

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摘要: 植物油脱臭馏出物中除了含有生育酚、甾醇等外, 还含有大量的游离脂肪酸。在天然生育酚的提取过程中产生大量的副产物脂肪酸甲酯。脂肪酸甲酯经过精制得到生物柴油, 使油脂脱臭馏出物得到综合利用。本文以棕榈油脱臭馏出物提取天然生育酚后的副产物为原料, 采用高真空蒸馏方法精制脂肪酸甲酯。考察了系统压力、温度及流量等操作条件的影响, 得出最佳蒸馏条件为: 系统压力越低对分离越有利, 温度 180℃, 流量 10~14ml/min, 脂肪酸甲酯 (FAMES) 回收率为 92.44%。分析了脂肪酸甲酯的各指标, 如游离甘油和总甘油含量、酸价、黏度、闪点、蒸馏温度等。结果表明精制后的脂肪酸甲酯质量指标达到了生物柴油的质量标准。

关键词: 生物柴油; 脱臭馏出物; 高真空蒸馏; 脂肪酸甲酯

中图分类号: TQ645.9; TE667

文献标识码: A

Preparation of Biodiesel from Palm Fatty Acid Distillate

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Abstract: Vegetable oil deodorizer distillates contain abundant free fatty acids besides tocopherols, phytosterols, etc. Fatty acid methyl esters (FAMES) were produced during the production of natural tocopherols. Biodiesel may be prepared by the purification of FAMES. In this paper, FAMES were purified by high vacuum distillation, using the by-product produced after the extraction of natural tocopherols from palm fatty acid distillates as the raw material. Operation conditions, e. g., pressure, temperature, and flow rate, were investigated. The lower the pressure is, the more beneficial to the separation. The optimal temperature and flow rate were 180℃ and 10-14 ml/min, respectively. The recovery of FAMES was 92.44%. The properties of FAMES, e. g., free glycerol content, total content of glycerol, acid value, viscosity, flashpoint, etc. were analyzed. The result showed that the purified FAMES might be used as biodiesel.

Key words: biodiesel; deodorizer distillate; high vacuum distillation; fatty acid methyl esters

引言

植物油脱臭馏出物是油脂加工脱臭过程产生的副产品。脱臭馏出物中富含天然维生素 E, 是天然维生素 E 的主要来源^[1], 天然维生素 E (生育酚) 具有许多生理功能、保健作用和抗氧化性, 在医药、食品、化妆品等行业中得到广泛的应用^[2,3]。浙江大学二次资源化工国家专业实验室开发成功了以脱臭馏出物为原料, 经过甲酯化、吸附分离提取高含量天然生育酚的工艺^[4]。然而, 在天然生育酚的提取过程中产生大量的副产物, 主要成分是脂肪酸甲酯。文献报道, 脂肪酸甲酯经过精制可以得到生物柴油^[5,6]。

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本文以棕榈油脱臭馏出物提取天然生育酚后的副产物为原料,采用高真空蒸馏方法精制脂肪酸甲酯,使棕榈油脱臭馏出物得到充分利用。考察了系统压力、温度及流量等操作条件的影响。

1 实验材料和方法

1.1 材料

1.1.1 实验设备 德国 U. I. C 公司薄膜蒸馏设备,型号 DSL5,处理量 0.5~2kg/h,蒸发面积:约 6dm²;蒸馏温度<200℃。

1.1.2 实验原料 棕榈油脱臭馏出物提取生育酚后的副产物,实验室自制。副产物中脂肪酸甲酯(FAMES)含量为 94.15%。

1.2 方法

1.2.1 蒸馏条件的选择 蒸馏温度和压力是影响蒸馏效果的两个重要因素。压力越低,物料越容易挥发到气相中,蒸馏温度也可适当降低。在进行刮膜式薄膜蒸馏时,进料速率将决定物料在蒸发壁面上的停留时间,直接影响分子蒸馏的效率和产品的纯度。刮板转速和进料温度也是影响蒸馏效果的另两个因素,原料黏度决定刮板转速和进料温度,由于棕榈油脱臭馏出物酯化物的黏度较小,因此刮板转速和进料温度的影响较小,不作为重点考查因素。

1.2.2 操作步骤 严格按照蒸馏设备的操作规程进行实验操作,试验前要检查系统的密封性,注意操作安全。将按最佳工艺条件精制的脂肪酸甲酯样品送到中国石化集团杭州炼油厂检测分析。

2 实验结果与讨论

薄膜蒸馏过程一般包括物料在加热表面上形成液膜、液膜表面的自由蒸发、轻分子向冷凝面运动和轻分子在冷凝面处被冷凝四个步骤^[7]。本文以薄膜蒸馏后轻重组分质量比 R (轻组分指在冷凝面冷凝部分,重组分指没有蒸发的部分)作为主要指标,来考察蒸馏压力、温度、进料流速等操作条件的影响,以得到最优的工艺条件。

2.1 系统压力的影响

系统压力越低,分子的挥发度越大,组分越容易被蒸出。本实验选用合适蒸馏温度、进料流速,通过调节真空泵后的放空阀开度来调节操作压力,考察轻、重组分质量比 R 的变化。

图 1 是在进料速率为 9.77ml/min,蒸馏温度为 180℃,刮板转速 300r/min,系统压力对轻重组分比 R 的影响。从图中可以看出,在相同蒸馏温度下,随着系统压力的升高,轻重组分比 R 降低。这是因为原料中较重的酯化物因压力升高而不再进入轻相中。因此,在确定的蒸馏温度下,系统压力越低对蒸出组分越有利。

2.2 蒸馏温度的影响

图 2 是在流量 6ml/min,系统压力 0.17mbar,刮板转速 300r/min,不同蒸馏温度下所得到的不同轻重组分比 R 。蒸除轻组分时,随着蒸馏温度的升高,轻重组分比 R 先是增加,到 170~180℃后,继续升高温度,轻重组分比 R 下降。这是因为开始时温度升高,蒸发量不断增大,分子在冷凝面冷凝的数量增大,轻重组分比增大;当温度升到一定程度(170~180℃)后,蒸发量进一步增大,气液分离不畅,部分轻组分夹带进入重相,因此造成 R 的降低。说明温度影响的复杂性。

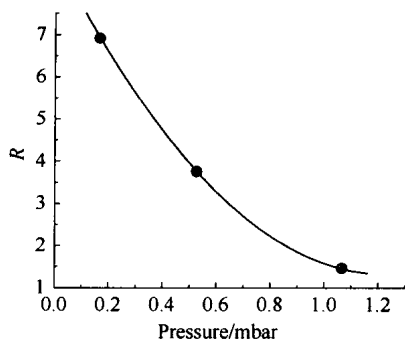


Fig. 1 Effect of Pressure on R
(R =light compositions/heavy compositions)

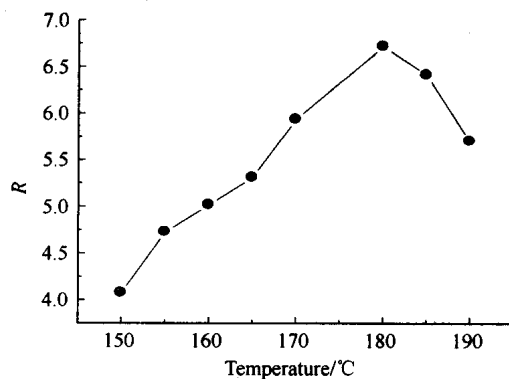


Fig. 2 Effect of temperature on R

2.3 进料流量的影响

在进行蒸馏时, 进料流量将决定物料在蒸发壁面上的停留时间, 直接影响蒸馏的效果和产品的纯度。

图 3 是在系统压力 0.17 mbar, 蒸馏温度为 180°C, 刮板转速 300 r/min, 不同进料流量下所得到的不同轻重组分比 R 。当流量较小时, 由于刮板式薄膜蒸馏装置结构上的特点, 由于蒸发量较小, 蒸发气体与冷凝面接触前, 已有部分轻组分在薄膜蒸馏设备顶部冷凝, 直接落入重组分中, 轻重比 R 较小; 当流量在 10~14 ml/min 之间时, 轻重相比 R 相对稳定, 说明进料流量在该区间对轻重相比 R 的影响不明显, 随着进料流量的继续增大, 物料在蒸发表面停留时间继续减小, 受热时间减小, 蒸出的轻组分量也随之减少, 重相中轻组分比例增大, 轻重比 R 减小。

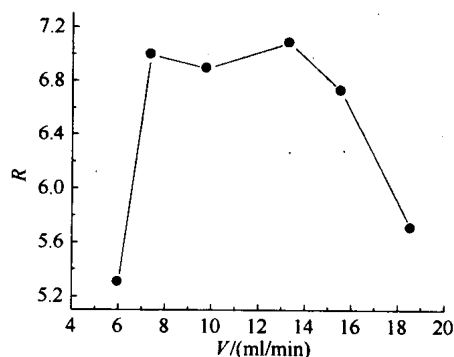


Fig. 3 Effect of flow rate on R

2.4 脂肪酸甲酯回收率

脂肪酸甲酯回收率计算公式:

$$R\text{-FAMES}\% = \frac{m \times R / (R+1) \times \text{FAMES}'\%}{m \times \text{FAMES}\%} \times 100\% = \frac{R \times \text{FAMES}'\%}{(R+1) \times \text{FAMES}\%} \times 100\%$$

式中, R 为蒸馏过程中轻重组分比; $\text{FAMES}\%$ 为原料中脂肪酸甲酯含量; $\text{FAMES}'\%$ 为轻相中脂肪酸甲酯含量。

按照最佳的蒸馏条件为: 蒸馏温度 180°C, 系统压力 0.17mbar, 进料流量 10~14ml/min, 刮板转速 300r/min。可以得到最佳的脂肪酸甲酯回收率为 92.44%。

2.5 生物柴油性能比较

表 1 列出了在最佳条件下得到的轻相组分的性质。

从表 1 可以看出, 本文制备的生物柴油与美国生物柴油标准 ASTM D6751-03S500 与欧洲 EN 14214 比较, 除了硫酸盐灰分含量 (0.0339%) 高于标准 (0.02%) 与游离甘油含量 (0.0392%) 略高于标准 (0.02%) 外, 其它都达到标准的要求。与我国 0# 柴油 (GB 252—2000) 比较, 除了凝固点 (15°C) 高于 0# 柴油 (4°C) 外, 其它的指标都满足标准的要求。因此, 利用棕榈油脱臭馏出物提取生育酚后的副产物为原料精制成脂肪酸甲酯可以作为生物柴油来使用。