ห้องสมุดงานวิจัย สำนักงานคณะกรรมการวิจัยแห่งชาติ
E42168

การสังเคราะห์อนุภาคทรงกลมคาร์บอนระดับไมโครเมตรโดยกระบวนการไฮโดรเทอร์มอลของแป้งดิบ

นายสาคร ราชหาด

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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

b00256913

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5170636121

SYNTHESIS OF CARBON MICROSPHERES BY HYDROTHERMAL PROCESS OF NATIVE STARCH

Mr. Sakhon Ratchahat

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2010
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Thesis Title	SYNTHESIS OF CARBON MICROSPHERES BY HYDROTHERMAL PROCESS OF NATIVE STARCH
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E 42168

สาคร ราชหาด : การสังเคราะห์อนุภาคทรงกลมคาร์บอนระดับไมโครเมตรโดยกระบวนการไฮโดรเทอร์มอลของแป้งดิบ. (SYNTHESIS OF CARBON MICROSPHERES BY HYDROTHERMAL PROCESS OF NATIVE STARCH) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : อาจารย์ ดร. อภินันท์ สุทธิธารธวัช, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม : รองศาสตราจารย์ ดร. ธวัชชัย ชรินพาณิชกุล, 143 หน้า.

การสังเคราะห์อนุภาคทรงกลมคาร์บอนระดับไมโครเมตร โดยกระบวนการไฮโดรเทอร์มอลของแป้งข้าวโพดในเครื่องปฏิกรณ์ออโตเคลบแบบกะ ใช้ทดลองเพื่อการควบคุมการกระจายตัวของขนาดอนุภาคคาร์บอน และเพื่อให้ทราบถึงกลไกการเกิดอนุภาคคาร์บอน อัตราการไฮโดรไลซ์ของแป้งข้าวโพดนั้นส่งผลอย่างมากต่อรูปร่างของอนุภาคาร์บอน การกระจายตัวของขนาดอนุภาค และผลได้ของอนุภาคคาร์บอน โดยการปรับเปลี่ยนเวลาในการทำปฏิกิริยาที่อุณหภูมิ 180 องศาเซลเซียสพบว่า อนุภาคคาร์บอนมีรูปร่างที่ไม่แน่นอนเพราะการโตของอนุภาคคาร์บอนนั้นยังไม่สมบูรณ์เนื่องจากปริมาณกลูโคสที่อยู่ในระบบนั้นยังมีปริมาณน้อยในตอนเริ่มต้น อย่างไรก็ตามอนุภาคคาร์บอนปฐมภูมินี้จะมีรูปร่างทรงกลม ขนาดใหญ่ขึ้น และขนาดใกล้เคียงกันมากขึ้น (8.0 ไมโครเมตร) เมื่อเพิ่มเวลาในทำปฏิกิริยามากขึ้นถึง 12 ชั่วโมง ในทางกลับกันเมื่ออุณหูมิในการทำปฏิกิริยาสูงขึ้น อนุภาคคาร์บอนปฐมภูมิจะมีขนาดประมาณเล็กเพียง 2.0 ไมโครเมตร เพราะอัตราการไฮโดรไลซ์ที่เร็ว แต่อนุภาคคาร์บอนปฐมภูมินี้จะเชื่อมติดกันกลายเป็นอนุภาคคาร์บอนทุติยภูมิขนาดใหญ่ นอกจากนั้นสามารถสังเคราะห์จากกระบวนการไฮโดรเทอร์มอลของกลูโคส ที่อนุภาคคาร์บอนปฐมภูมิมีขนาดเล็กประมาณ 0.12 ไมโครเมตร เพราะปริมาณกลูโคสที่มีมากในตอนต้นของปฏิกิริยานั้นกลูโคสจะเกิดเป็นหลายๆ นิวเคลียสของอนุภาคคาร์บอนขึ้นพร้อมกัน กล่าวคือการเกิดนิวเคลียสของอนุภาคคาร์บอนมีบทบาทมากกว่าการโตของอนุภาคคาร์บอนจึงทำให้อนุภาคนั้นมีขนาดเล็ก ปฏิกิริยาที่เกิดระหว่างกระบวนการไฮโดรเทอร์มอลนั้น ประกอบไปด้วยการไฮโดรไลซิสของแป้งข้าวโพดไปเป็นกลูโคส จากนั้นกลูโคสจะถูกดีไฮเดรชัน สุดท้ายเกิดพอลิเมอไรเซชันและอะโรมาไทเซชันกลายเป็นอนุภาคคาร์บอน ซึ่งปฏิกิริยาเหล่านี้สามารถทำนายได้จากแผนภาพแวนเครบเวอเลน และผลวิเคราะห์ฟูเรียร์ทรานสฟอร์มอินฟาเรด นอกจากนั้นแล้ว ผลวิเคราะห์จากกล้องอิเล็กตรอนแบบส่องผ่านและผลวิเคราะห์ฟูเรียร์ทรานสฟอร์มอินฟาเรด แสดงให้เห็นว่า องค์ประกอบของอนุภาคคาร์บอนนี้ประกอบไปด้วยวงอะโรมาติกคาร์บอนอัดตัวกันแน่นเป็นแกนกลางและมีเปลือกนอกที่มีหมู่ฟังก์ชันที่ว่องไว เพื่อที่จะเข้าใจถึงกลไกการเกิดอนุภาคมากขึ้น ตัวแปรจลนพลศาสตร์หรือค่าคงที่ของการเกิดปฏิกิริยาถูกคำนวณได้จาก การวัดปริมาณความเข้มข้นของสารมัธยันตร์ในแต่ละช่วงเวลาการเกิดปฏิกิริยาในเครื่องปฏิกรณ์ออโตเคลบแบบกะ โดยมีสมมติฐานว่าทุกปฏิกิริยาที่เกิดขึ้นเป็นปฏิกิริยาอันดับหนึ่ง พบว่าแบบจำลองกลไกการเกิดอนุภาคนี้สอดคล้องกับ ข้อมูลการไฮโดรเทอร์มอลของกลูโคสเป็นอย่างดี อย่างไรก็ตาม ผลการทดลองในกระบวนการไฮโดรเทอร์มอลของแป้งข้าวโพดนั้น ยังไม่เป็นไปตามสมมติฐานกลไกการเกิดปฏิกิริยาอันดับหนึ่ง เนื่องจากแป้งดิบมีโครงสร้างที่ถูกไฮโดรไลซ์ได้ยาก

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก
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5170636121 : MAJOR CHEMICAL ENGINEERING

KEYWORDS : CARBON MICROSPHERES / STARCH / KINETICS

SAKHON RATCHAHAT : SYNTHESIS OF CARBON MICROSPHERES BY HYDROTHERMAL PROCESS OF NATIVE STARCH. ADVISOR : APINAN SOOTTITANTAWAT, D.Eng. CO-ADVISOR : ASSOC. PROF. TAWATCHAI CHARINPANITKUL, D.Eng. 143 pp.

E 42168

Synthesis of carbon microspheres (CMSs) with controlled particle size distributions using hydrothermal process of native and modified corn starch has been investigated systematically in a batch reactor. Formation mechanisms of CMSs were also proposed. Hydrolyzed rates of native corn starch were demonstrated to have strong effects on morphology, particle size distributions, uniformity and yields of the synthesized CMSs. By varying the reaction time between 0 and 24 hours at 180°C, CMSs were irregular shape because the CMSs development still was not complete with the small amount of glucose from the hydrolysis reaction in the system at the beginning of the reaction. Nevertheless, the CMSs became uniform and large size with primary particles of 8.0 μm when the reaction time increased to 12 hours. On the other hand, primary particles of 2.0 μm were obtained at high reaction temperature (at 220°C) because of the rapid hydrolyzed rate but the CMSs were likely to aggregate secondary particles. In addition, the smallest primary particles of 0.12 μm were obtained from hydrothermal process of glucose because high quantity of glucose in the system simultaneously formed many nuclei of CMSs. Therefore, the nuclei formation plays an important role than the growth mechanism and the CMSs were the smallest size than others. Proposed reactions during hydrothermal process composed of hydrolysis of native corn starch to glucose, subsequently dehydration of glucose, finally polymerization and aromatization to form the CMSs which were predicted from van Krevenlen chart and FT-IR results. Moreover, the results from TEM observations and FT-IR analysis revealed that the structure of the synthesized CMSs mainly consisted of condensed aromatic-carbon-ring compounds as a core and reactive hydrophilic compounds as a shell. To gain an insight into the CMS formation mechanisms, concentrations of intermediates formed during the hydrothermal process were determined at different times for the determination of reaction kinetic parameters. It was found that the experimental data from hydrothermal process of glucose, could be fitted with the assuming pseudo-first-order kinetic model. The proposed reaction pathway could also be verified with the experimental results. Nevertheless, the hydrothermal treatment results of native corn starch deviated from the first-order kinetic model because of its difficult to be hydrolyzed.

Department : Chemical Engineering Student's Signature Sakhon Ratchahat
Field of Study : Chemical Engineering Advisor's Signature A. Soottitantawat
Academic Year : 2010 Co-Advisor's Signature

ACKNOWLEDGEMENTS

First of all, I would like to acknowledge the Centennial of Chulalongkorn University for partial financial support throughout my study. I am very thankful for this support.

I would like to express my deep gratitude to my supervisor, Dr. Apinan Soottitantawat for his guidance and patience in the past two years of my study. I appreciate his supervising technique which made me more confident and independent in my research. Thank you very much indeed.

I am deeply indebted to Assoc. Prof. Tawatchai Charinpanitkul for his kind help all the way to study completion. Without his support and inspiration, I do not think I would be able to make it.

I am grateful to Asst. Prof. Varong Pavarajarn, Prof. Suttichai Assabumrungrat, Asst. Prof. Joongjai Panpranot, Dr. Kajornsak Faungnawakij and Assoc. Prof. Prasert Pavasant for their time to time advice and guidance in my study.

I would like to thank Dr. Benjapol Kongsombut for his advice and Miss Siriporn Monchayapisut for her advice and help.

I would like to thank Miss Pailin Penbunditkul, Mr. Worachate Kongthon and Miss Saran Kornbongkojmas for their help

I would like to thank all the members in Center of Excellence in Particle Technology for accompanying, cheering, discussing and helping me in any situations during the period of my study here.

Last but not least, I would like to express my greatest thanks to my family who always are there for me. Without any doubt, my Master degree belongs to them.

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NOMENCLATURE

[CMSs]	Carbon microspheres concentration [mol-C/L]
[fructose]	Fructose concentration [mol-C/L]
[furfural]	Furfural concentration [mol-C/L]
[glucose]	Glucose concentration [mol-C/L]
[5-HMF]	5-HMF concentration [mol-C/L]
k_{5c}	Rate constant for the CMSs formation from 5-HMF $[(\text{mol-C/L})^{-1}\cdot s^{-1}]$
k_{5fc}	Rate constant for the polymerization between 5-HMF and furfural to CMSs $[(\text{mol-C/L})^{-1}\cdot s^{-1}]$
k_{5t}	Rate constant for the 5-HMF decomposition $[s^{-1}]$
k_{5tc}	Rate constant for the polymerization between 5-HMF and TOC to CMSs $[(\text{mol-C/L})^{-1}\cdot s^{-1}]$
k_{5tfc}	Rate constant for the polymerization among 5-HMF, furfural, and TOC to CMSs $[(\text{mol-C/L})^{-2}\cdot s^{-1}]$
k_{f5}	Rate constant for the fructose dehydration to 5-HMF $[s^{-1}]$
k_{ffu}	Rate constant for the fructose dehydration to furfural $[s^{-1}]$
k_{ft}	Rate constant for the fructose decomposition $[s^{-1}]$
k_{ftc}	Rate constant for the polymerization between furfural and TOC to CMSs $[(\text{mol-C/L})^{-1}\cdot s^{-1}]$
k_{fuc}	Rate constant for the furfural polymerization to CMSs $[s^{-1}]$
k_{fut}	Rate constant for the furfural decomposition $[s^{-1}]$
k_{g5}	Rate constant for the glucose dehydration to 5-HMF $[s^{-1}]$

k_{gf}	Rate constant for the glucose isomerization to fructose [s^{-1}]
k_{gfu}	Rate constant for the glucose dehydration to furfural [s^{-1}]
k_{gt}	Rate constant for the glucose decomposition [s^{-1}]
k_{tc}	Rate constant for the CMSs formation from liquid product [$(mol\text{-}C/L)^{-1}\cdot s^{-1}$]
K_w	Dissociation constant of water [$(mol/kg)^2$]
r^2	Determination coefficient [dimensionless]
t	Reaction time (reaction time), or the sampling time in equation 4.1 [s]
T	Reaction temperature, or the room temperature during the gas product sampling in equation 4.1 [K, °C]
TOC	Lumped/unspecified liquid products (in the context of product yield/concentration)
[TOC]	TOC concentration [mol-C/L]

Greek letters

ε	Dielectric constant of water [dimensionless]
ρ_c	Critical density of water [kg/m^3]

Abbreviations

AL	amylose
AP	amylopectin
BDO	1,4-Benzenediol
BTO	1,2,4-Benzenetriol
CR	native corn starch

FT-IR	Fourier Transform-Infrared Spectroscopy
GC	glucose
5-HMF	5-Hydroxymethylfurfural
HPLC	High Performance Liquid Chromatography
IC	Inorganic Carbon
LSE	Least Square of Error
NPOC	Non-Purgeable Organic Carbon
SEM	Scanning Electron Microscope
TOC	Total Organic Carbon (analytical method context)
TOC-IC	Total Organic Carbon-Inorganic Carbon