รายงานวิจัยฉบับสมบูรณ์

โครงการตัวเร่งปฏิกิริยาไฮโดรเทอร์มอลคาร์บอนที่เติมหมู่ฟังก์ชันของกรดเพื่อการผลิตไบโอดีเซลและเชื้อเพลิงเหลวจากชีวมวล

สัญญาเลขที่ RSA5880047

โดย นางสาว อาทิวรรณ โชติพฤกษ์ และคณะ

มิถุนายน 2561

รายงานวิจัยฉบับสมบูรณ์

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คณะผู้วิจัย **สังกัด**

นางสาวอาทิวรรณ โชติพฤกษ์ **ภาควิชาวิศวกรรมเคมี จุฬาลงกรณ์มหาวิทยาลัย**

สนับสนุนโดยสำนักงานคณะกรรมการอุดมศึกษา และสำนักงานกองทุนสนับสนุนการวิจัย

(ความเห็นในรายงานนี้เป็นของผู้วิจัย สกอ.และสกว.ไม่จำเป็นต้องเห็นด้วยเสมอไป)

บทคัดย่อ

รหัสโครงการ RSA5880047

ชื่อโครงการ ตัวเร่งปฏิกิริยาไฮโดรเทอร์มอลคาร์บอนที่เติมหมู่ฟังก์ชันของกรดเพื่อการผลิตไบโอดีเซลและเชื้อเพลิงเหลวจากชีวมวล

ชื่อนักวิจัย **ศ.ดร.อาทิวรรณ โชติพฤกษ์**
อีเมล **artiwan.sh@chula.ac.th**
ระยะเวลาโครงการ **6 กรกฎาคม 2558 ถึง 5 กรกฎาคม 2561**

งานวิจัยนี้มีจุดมุ่งหมายเพื่อศึกษาการเตรียมตัวเร่งปฏิกิริยาไฮโดรเทอร์มอลคาร์บอนจากรำข้าวและน้ำตาลกลูโคสเพื่อใช้ในการแปรสภาพชีวมวลเป็น 5-ไฮดรอกซีเมทิลเฟอฟูรอล โดยพิจารณาผลของอุณหภูมิ (180-250 องศาเซลเซียส) และเวลา (1-8 ชั่วโมง) ในการคาร์บอไนเซชันต่อปริมาณและลักษณะทางเคมีของ HTC หลังจากนั้นทำการติดหมู่ซัลโฟนิก HTC ด้วยกรดซัลฟูริกเพื่อเตรียมตัวเร่งปฏิกิริยา HTC-SO_3H และทำการทดสอบความเสถียรของตัวเร่งปฏิกิริยาโดยพิจารณาปริมาณของผลิตภัณฑ์จากการแปรสภาพชีวมวลที่ถูกชะด้วยน้ำที่สภาวะการแปรสภาพชีวมวล จากการทดสอบพบว่า ไม่มีปริมาณ 5-ไฮดรอกซีเมทิลเฟอฟูรอล และเฟอฟูรอล และมีกรดลิวูลินิกและกรดฟอร์มิกปริมาณน้อย ถูกชะออกมาจาก HTCDRB-SO_3H ที่สังเคราะห์จาก HTCDRB ที่เตรียมจากการคาร์บอไนเซชันที่อุณหูมิ 220 องศาเซลเซียส เป็นเวลา 3 ชั่วโมง แสดงให้เห็นว่าสภาวะดังกล่าวเหมาะสมสำหรับการเตรียม HTCDRB-SO_3H เมื่อเปรียบเทียบเสถียรภาพของ HTCDRB-SO_3H และ HTCG-SO_3H ที่เตรียมที่สภาวะเดียวกัน พบว่า HTCG-SO_3H มีเสถียรภาพน้อยกว่า อย่างไรก็ตามยังมีการศึกษาการปรับปรุงเสถียรภาพของ HTCG-SO_3H โดยการเพิ่มเวลาในการคาร์บอไนเซชัน (6-24 ชั่วโมง) พบว่า HTCG ที่สภาวะต่างๆของการคาร์บอไนเซชันมีลักษณะทางเคมีและโครงสร้างเหมือนกัน ส่วนของเหลวที่ได้หลังผ่านไฮโดรเทอร์มอลคาร์บอไนเซชันสามารถบอกความเสถียรของ HTCG ได้ โดยสภาวะที่เหมาะสมในการเตรียมคาร์บอนจากน้ำตาลกลูโคสให้มีความเสถียร คือ ไฮโดรเทอร์มอลคาร์บอไนเซชันที่อุณหภูมิ 220 องศาเซลเซียสเป็นเวลา 6 ชั่วโมง นอกจากนี้ตัวเร่งปฏิกิริยาที่เตรียมจากสภาวะที่เหมาะสมมีความสามารถในการเร่งปฏิกิริยาไฮโดรไลซิสของเซลลูโลสและดีไฮเดรชันของน้ำตาลฟลุ๊กโตสได้ค่อนข้างสูง และตัวเร่งปฏิกิริยานี้สามารถนำไปประยุกต์ใช้ในกระบวนการต่างๆได้ เช่น การแปรสภาพของเซลลูโลสและลิกนินไปเป็นสารที่มีมูลค่า และการผลิตไบโอดีเซล

Abstract

This research investigated the preparation of hydrothermal carbon-based catalysts (HTC-SO_3H) derived from defatted rice bran (DRB) and glucose for biomass conversion to 5-hydroxymethylfurfural (HMF). Firstly, the effects of hydrothermal carbonization conditions: temperature (180-250 °C) and time (1-8 h) on the yield and the chemical characteristics of the hydrothermal carbons (HTCs) were investigated. The HTCs were then sulfonated with sulfuric acid to obtain HTC-SO_3H catalysts. The stability of the catalysts was evaluated based on the amount of biomass conversion products leached into the water at a specified biomass conversion condition. Since no HMF and furfural, and only small amounts of levulinic acid and formic acid, were leached from DRB derived HTC-SO_3H (HTCDRB-SO_3H) catalyst synthesized from the DRB derived HTC (HTCDRB) prepared at the carbonization condition of 220 °C for 3 h, this condition was suggested to be a suitable carbonization condition for the preparation. Compared with HTCDRB-SO_3H, the glucose derived HTC-SO_3H (HTCG-SO_3H) prepared at the same condition showed the lower stability. The stability improvement of HTCG-SO_3H was then studied at the longer hydrothermal carbonization time (6-24 h). While glucose derived HTCs (HTCGs) prepared at all conditions exhibited similar chemical and structural characteristics, examination of liquid fractions from hydrothermal carbonization suggested the suitable hydrothermal carbonization condition to be at 220 °C and 6 h. Sulfonated catalysts prepared at the proposed conditions were shown to promote cellulose hydrolysis and fructose dehydration with relatively high reactivity, and it can apply in process of cellulose conversion, lignin depolymerization, and biodiesel production.

Executive Summary

ตัวเร่งปฏิกิริยาวิวิธพันธ์จำพวกคาร์บอนกำลังได้รับความสนใจอย่างแพร่หลายเนื่องจาก เป็นตัวเร่งปฏิกิริยาที่มีราคาถูกและมีประสิทธิภาพสูง สามารถเตรียมได้จากวัตถุดิบที่มีราคาถูก เช่น น้ำตาล สารประกอบอะโรมาติก เรซิน ไบโอชาร์ และลิกนิน กระบวนการเตรียมไม่ยุ่งยาก อีกทั้งยังสามารถสังเคราะห์ตัวเร่งปฏิกิริยาที่มีความเป็นกรดสูงและมีเสถียรภาพทางความร้อนสูงซึ่งเหมาะสมกับการใช้งานในกระบวนการที่หลากหลาย เพื่อผลิตเชื้อเพลิงและสารเคมีชีวภาพ งานวิจัยมีวัตถุประสงค์เพื่อพัฒนาตัวเร่งปฏิกิริยาจากทรัพยากรเหลือใช้ทางการเกษตรของประเทศ เพื่อนำไปผลิตสารมูลค่าเพิ่มในกระบวนการต่างๆ เช่นการผลิตไบโอดีเซลและการแปรสภาพชีวมวล ในส่วนแรกคำถึงการพัฒนาตัวเร่งปฏิกริยาด้วยกระบวนการไฮโดรเทอร์มอลคาร์บอไนเซชัน เพื่อเตรียมตัวเร่งปฏิกิริยาให้มีความเหมาะสมต่อการนำไปประยุกต์ใช้ และในส่วนที่สองเป็นการนำตัวเร่งปฏิกิริยาดังกล่าวไปใช้ในกระบวนการผลิตไบโอดีเซล และการแปรสภาพชีวมวลเป็นสารที่มีมูลค่า

เนื้อหางานวิจัย

บทนำ

ในปัจจุบันมีการศึกษาวิจัยเกี่ยวกับการพัฒนาตัวเร่งปฏิกิริยาวิวิธพันธ์ที่มีราคาถูกและมีประสิทธิภาพสูงเพื่อใช้ทดแทนตัวเร่งปฏิกิริยาเอกพันธ์อย่างกว้างขวางเนื่องจากประโยชน์ในแง่ของความสะดวกในการแยกและนำกลับมาใช้ใหม่ ในบรรดาตัวเร่งปฏิกิริยาวิวิธพันธ์ที่มีการพัฒนาในปัจจุบัน ตัวเร่งปฏิกิริยาวิวิธพันธ์จำพวกคาร์บอนที่มีความเป็นกรดสูงกำลังได้รับความสนใจอย่างแพร่หลายเนื่องจากสามารถเตรียมได้จากวัตถุดิบที่มีราคาถูก เช่น น้ำตาล สารประกอบอะโรมาติก เรซิน ไบโอชาร์ และลิกนิน กระบวนการเตรียมไม่ยุ่งยาก อีกทั้งยังสามารถสังเคราะห์ตัวเร่งปฏิกิริยาที่มีความเป็นกรดสูงและมีเสถียรภาพทางความร้อนสูงซึ่งเหมาะสมกับการใช้งานในกระบวนการที่หลากหลายเพื่อผลิตเชื้อเพลิงและสารเคมีชีวภาพ งานวิจัยนี้มีเป้าหมายเพื่อพัฒนาตัวเร่งปฏิกิริยาวิวิธพันธ์จำพวกคาร์บอนที่มีความเป็นกรดสูงจากแหล่งชีวมวลภายในประเทศด้วยกระบวนการไฮโดรเทอร์มอลซึ่งเป็นกระบวนการที่มีความเป็นมิตรต่อสิ่งแวดล้อมสูง ทั้งยังสามารถเตรียมตัวเร่งปฏิกิริยาในปริมาณสูงได้อย่างรวดเร็ว ในรายละเอียดแล้ว โครงการนี้ทำการศึกษาหาสภาวะที่เหมาะสมในการเตรียมตัวเร่งปฏิกิริยาด้วยกระบวนการไฮโดรเทอร์มอลคาร์บอไนเซชัน ที่มีต่อคุณสมบัติของตัวเร่งปฏิกิริยาที่เตรียมได้ เพื่อให้สามารถพัฒนาตัวเร่งปฏิกิริยาที่มีความเหมาะสมต่อการใช้งานในอุตสาหกรรมเคมีชีวภาพประเภทต่างๆ อย่างหลากหลาย

อนึ่งอุตสาหกรรมเคมีชีวภาพเกี่ยวข้องกับกระบวนการในการผลิตเชื้อเพลิงชีวภาพ และสารเคมีที่มีมูลค่าจากวัตถุดิบทางการเกษตรด้วยวิธีการที่เป็นมิตรกับสิ่งแวดล้อม ซึ่งเป็นกระบวนการที่มีศักยภาพอย่างยิ่งสำหรับประเทศไทยซึ่งมีพื้นฐานทางเกษตรกรรมและอุตสาหกรรมที่เกี่ยวเนื่อง โครงการวิจัยนี้มีวัตถุประสงค์ในการพัฒนากระบวนการในการผลิตเชื้อเพลิงชีวภาพ และสารเคมีที่มีมูลค่าจากวัตถุดิบทางการเกษตรของประเทศโดยจะดำเนินการวิจัยภายใต้กระบวนการหลัก 2 ประเภท กระบวนการแรกคือการผลิตเชื้อเพลิงไบโอดีเซลจากวัตถุดิบจำพวกปาล์มน้ำมันซึ่งเป็นวัตถุดิบที่สำคัญของประเทศที่ถูกนำมาใช้เพื่อผลิตไบโอดีเซลอย่างกว้างขวางในปัจจุบัน โดยทั่วไปแล้วน้ำมันปาล์มจะมีองค์ประกอบของกรดไขมันอิสระประเภทต่างๆ อยู่ในสัดส่วนที่สูง ซึ่งกรดไขมันอิสระเหล่านี้ต้องถูกแยกออกหรือบำบัดก่อนการแปรสภาพนำน้ำมันปาล์มเป็นไบโอดีเซล การแปรสภาพกรดไขมันอิสระเหล่านี้เป็นสารประกอบเมทิลเอสเทอร์ควบคู่ไปกับการใช้น้ำมันปาล์มดิบและน้ำมันปาล์มที่ผ่านกระบวนการแยกจะช่วยลดค่าใช้จ่ายของกระบวนการผลิตไบโอดีเซลและทำให้ราคาไบโอดีเซลที่ผลิตได้สามารถแข่งขันได้กับเชื้อเพลิงฟอสซิล แต่เทคโนโลยีการผลิตไบโอดีเซลด้วยตัวเร่งปฏิกิริยาแบบเอกพันธ์ที่ใช้ในปัจจุบันยังคงมีข้อจำกัดเนื่องจากไม่สามารถใช้ได้กับวัตถุดิบที่มีกรดไขมันอิสระและการไม่สามารถนำตัวเร่งปฏิกิริยากลับมาใช้ใหม่ โครงการวิจัยนี้จึงมุ่งเน้นในการพัฒนาข้อจำกัดดังกล่าวโดยการพัฒนาตัวเร่งปฏิกิริยาวิวิธพันธ์จำพวกคาร์บอนที่มีความเป็นกรดสูงซึ่งสามารถใช้ได้กับวัตถุดิบที่มีกรดไขมันอิสระสูงและนำมากลับมาใช้ใหม่ได้ ซึ่งจะเป็นการเพิ่มความคุ้มค่าทางเศรษฐศาสตร์ในกระบวนการผลิตไบโอดีเซลในอนาคต กระบวนการที่สองคือการแปรสภาพวัสดุชีวมวลไปเป็นสารเคมีมูลค่าสูง ทั้งนี้ในบริบทของประเทศไทยซึ่งเป็นประเทศเกษตรกรรมมีวัสดุชีวมวลเหลือใช้หลากหลายประเภทเป็นจำนวนมาก การนำวัสดุชีวมวลเหล่านี้มาใช้เป็น

สารตั้งต้นในการสังเคราะห์สารเคมีมีมูลค่าจะมีส่วนช่วยประเทศชาติในการเพิ่มความมั่นคงด้านเศรษฐศาสตร์อย่างมีนัยสำคัญ ทั้งนี้กระบวนการแปรสภาพชีวมวลที่จะดำเนินการในโครงการนี้คือ กระบวนการไฮโดรไลซิสชีวมวลเป็นน้ำตาล และกระบวนการดีไฮเดชันน้ำตาลที่ได้ไปเป็นสารประกอบฟูแลนและกรดอินทรีย์ชนิดต่างๆ เนื่องจากกระบวนการเหล่านี้ต้องอาศัยตัวเร่งปฏิกิริยาจำพวกกรดในการเร่งปฏิกิริยา และผลิตภัณฑ์ที่กล่าวมาเป็นผลิตภัณฑ์สำคัญที่มีความจำเป็นต่ออุตสาหกรรมเคมีต่างๆ ของประเทศ

ผลของงานวิจัยนี้นำไปสู่การพัฒนาตัวเร่งปฏิกิริยาที่มีศักยภาพต่อกระบวนการดังกล่าว เพื่อเพิ่มมูลค่าให้กับชีวมวลซึ่งเป็นวัตถุดิบที่เป็นผลพลอยได้ทางการเกษตร อีกทั้งยังเป็นการสร้างองค์ความรู้ใหม่ ที่สามารถต่อยอดใช้ประโยชน์ในภาคอุตสาหกรรมได้ต่อไป

วัตถุประสงค์

1 เตรียมตัวเร่งปฏิกิริยาไฮโดรเทอร์มอลคาร์บอนจากสารตั้งต้นชนิดต่างๆ โดยหาสภาวะที่เหมาะสมในการเตรียมตัวเร่งปฏิกิริยาด้วยวิธีดังกล่าว
2 ศึกษาลักษณะสมบัติของตัวเร่งปฏิกิริยาที่เตรียมขึ้น
3 ทดสอบตัวเร่งปฏิกิริยากับปฏิกิริยาการเปลี่ยนชีวมวลให้เป็นน้ำตาล ฟิวแรน และอื่นๆ
4 ทดสอบตัวเร่งปฏิกิริยากับปฏิกิริยาการผลิตไบโอดีเซล
5 ศึกษาสภาวะที่เหมาะสมต่อการเกิดปฏิกิริยาในข้อ 3 และ 4

ระเบียบวิธีวิจัย

1 รวบรวมเอกสารวิจัย
2 ทดสอบวิธีการวิเคราะห์สาร
3 ทดลองการเตรียมคาร์บอนด้วยวิธีการไฮโดรเทอร์มอลคาร์บอไนเซชัน
4 ทดลองการติดหมู่กรดซัลโฟนิกบนคาร์บอนด้วยกระบวนการซัลโฟเนชัน
5 ทดสอบวิเคราะห์ลักษณะทางกายภาพ ทางเคมี และความสามารถในการเร่งปฏิกิริยาของตัวเร่งปฏิกิริยา
6 สรุปผล ทำรายงานและเตรียมผลงานตีพิมพ์ในวารสารนานาชาติ

ผลที่ได้จากงานวิจัย

ผลที่ได้จากงานวิจัยในโครงการนี้ ได้รับการตีพิมพ์ในวารสารวิชาการระดับนานาชาติจำนวน 5 เรื่อง (1-5) และ อยู่ระหว่างการรอตอบรับตีพิมพ์ในวารสารวิชาการระดับนานาชาติจำนวน 1 เรื่อง (6) ดังต่อไปนี้

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2. Wataniyakul P., Boonnoun P., Quitain A.T., Mitsuru S., Kida T. Laosiripoj N., **Shotipruk A.** Preparation of hydrothermal carbon as catalyst support for conversion of biomass to 5-hydromethylfurfural, Catalysis Communications 104, 2018, 41-48.
3. Suriyachai N., Champreda V., Sakdaronnarong C., **Shotipruk A.**, Laosiripojana N. Sequential organosolv fractionation/hydrolysis of sugarcane bagasse: The coupling use of heterogeneous H_3PO_4-activated carbon as acid promoter and hydrolysis catalyst, Renewable Energy 113, 2017, 1141-1148.
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6. Boonyakarn T., Wataniyakul P., Boonnoun P., Quitain A.T. Kida T., Sasaki M., Laosiripojana N., Jongsomjit B., **Shotipruk A.** Enhanced levulinic acid production from cellulose by combined brønsted hydrothermal carbon and lewis acid catalysts (Submitted in Catalysis Communications).

เรื่องที่ 1-2 เป็นการพัฒนาตัวเร่งปฏิกิริยาวิวิธพันธ์จำพวกคาร์บอนแบบกรดจากน้ำตาลกลูโคสและรำข้าวสกัดน้ำมัน ด้วยกระบวนการไฮโดรเทอร์มอลคาร์บอไนเซชัน เรื่องที่ 3 5 และ 6 เป็นการประยุกต์ใช้ตัวเร่งปฏิกิริยาในกระบวนการแปรสภาพชีวมวลเป็นสารที่มีมูลค่า เรื่องที่ 4 เป็นการพัฒนากระบวนการผลิตไบโอดีเซลโดยการใช้ไมโครเวฟร่วมกับตัวเร่งปฏิกิริยาวิวิธพันธ์จำพวกคาร์บอนแบบกรด โดยศึกษาเบื้องต้นเกี่ยวกับผลของไมโครเวฟต่อการผลิตไบโอดีเซล

เรื่องที่ 1

ชื่อเรื่อง (อังกฤษ) Preparation of Hydrothermal Carbon Acid Catalyst from Defatted Rice Bran

ชื่อเรื่อง (ไทย) การเตรียมตัวเร่งปฏิกิริยาไฮโดรเทอร์มอลคาร์บอนแบบกรดจากรำข้าวสกัดน้ำมัน

ชื่อผู้เขียน (ไทย) ปิยาภรณ์ วทานิยะกุล[1], ปณัฐพงศ์ บุญนวล[2], อาร์มานโด ที คิตาอิน[3], เทสสึยะ คิดะ[3], นวดล เหล่าศิริพจน์[4] และอาทิวรรณ โชติพฤกษ์[1]

ชื่อหน่วยงาน/สังกัดของผู้เขียน (ไทย)

1. หน่วยปฏิบัติการวิศวกรรมเคมีเพื่อเพิ่มมูลค่าของทรัพยากรทางชีวภาพ ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย กรุงเทพ 10330
2. ภาควิชาวิศวกรรมอุตสาหการ คณะวิศวกรรมศาสตร์ มหาวิทยาลัยนเรศวร พิษณุโลก 65000
3. ภาควิชาชีวเคมีและเคมีประยุกต์ มหาวิทยาลัยคุมาโมโตะ ญี่ปุ่น
4. บัณฑิตวิทยาลัยร่วมด้านพลังงานและสิ่งแวดล้อม มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี กรุงเทพ 10140

ชื่อวารสาร (อังกฤษ) Industrial Crops and Products

บทคัดย่อ (ไทย)

งานวิจัยนี้มีจุดมุ่งหมายเพื่อศึกษาการเตรียมตัวเร่งปฏิกิริยาคาร์บอนแบบกรดจากรำข้าวสกัดน้ำมันด้วยกระบวนการไฮโดรเทอร์มอลคาร์บอไนเซชัน และการติดหมู่ซัลโฟนิกด้วยกรดซัลฟูริก โดยพิจารณาผลของอุณหภูมิ (180-250 องศาเซลเซียส) และเวลา (1-8 ชั่วโมง) ในการคาร์บอไนเซชันต่อปริมาณและลักษณะทางเคมีของไฮโดรเทอร์มอลคาร์บอน นอกจากนี้ยังศึกษาผลของการคาร์บอไนเซชันต่อลักษณะทางเคมีและความเสถียรของตัวเร่งปฏิกิริยาคาร์บอนแบบกรดจากรำข้าวสกัดน้ำมัน โดยพิจารณาปริมาณของผลิตภัณฑ์จากการแปรสภาพชีวมวลที่ถูกชะด้วยน้ำที่สภาวะการแปรสภาพชีวมวล จากการทดสอบพบว่า ไม่มีปริมาณ 5-ไฮดรอกซีเมทิลเฟอฟูรอลและเฟอฟูรอล และมีกรดลิวูลินิก (ร้อยละ 1.75 โดยมวล) และกรดฟอร์มิก (ร้อยละ 0.42 โดยมวล) ปริมาณน้อย ถูกชะออกมาจากตัวเร่งปฏิกิริยาคาร์บอนแบบกรดจากรำข้าวสกัดน้ำมันที่สังเคราะห์จากคาร์บอนที่เตรียมจากการคาร์บอไนเซชันที่อุณหูมิ 220 องศาเซลเซียส เป็นเวลา 3 ชั่วโมง แสดงให้เห็นว่าสภาวะดังกล่าวเหมาะสมสำหรับการเตรียมตัวเร่งปฏิกิริยาคาร์บอนแบบกรดจากรำข้าวสกัดน้ำมัน เมื่อเปรียบเทียบเสถียรภาพของตัวเร่งปฏิกิริยาคาร์บอนแบบกรดจากรำข้าวสกัดน้ำมัน กับตัวเร่งปฏิกิริยาคาร์บอนแบบกรดจากน้ำตาลกลูโคสที่เตรียมที่สภาวะเดียวกัน พบว่าตัวเร่งปฏิกิริยาคาร์บอนแบบกรดจากรำข้าวสกัดน้ำมันมีเสถียรภาพมากกว่า นอกจากนี้ตัวเร่งปฏิกิริยาคาร์บอนแบบกรดจากรำข้าวสกัดน้ำมันสามารถสนับสนุนการไฮโดรไลซิสของเซลลูโลสได้ค่อนข้างสูง เมื่อเปรียบเทียบกับตัวเร่งปฏิกิริยา Amberlyst 16 wet

เรื่องที่ 2

ชื่อเรื่อง (อังกฤษ) Preparation of hydrothermal carbon as catalyst support for conversion of biomass to 5-hydroxymethylfurfural

ชื่อเรื่อง (ไทย) การเตรียมไฮโดรเทอร์มอลคาร์บอนซึ่งเป็นตัวรองรับตัวเร่งปฏิกิริยาสำหรับการแปรสภาพชีวมวลเป็น 5-ไฮดรอซีเมททิลเฟอร์ฟูรอล

ชื่อผู้เขียน (ไทย) ปิยาภรณ์ วทานิยะกุล[1], ปณัฐพงศ์ บุญนวล[2], อาร์มานโด ที คิตาอิน[3], เทสสึยะ คิดะ[3], มิตซูรุ ซาซากิ[3], นวดล เหล่าศิริพจน์[4] และอาทิวรรณ โชติพฤกษ์[1]

ชื่อหน่วยงาน/สังกัดของผู้เขียน (ไทย)

1. หน่วยปฏิบัติการวิศวกรรมเคมีเพื่อเพิ่มมูลค่าของทรัพยากรทางชีวภาพ ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย กรุงเทพ 10330
2. ภาควิชาวิศวกรรมอุตสาหการ คณะวิศวกรรมศาสตร์ มหาวิทยาลัยนเรศวร พิษณุโลก 65000
3. ภาควิชาชีวเคมีและเคมีประยุกต์ มหาวิทยาลัยคุมาโมโตะ ญี่ปุ่น
4. บัณฑิตวิทยาลัยร่วมด้านพลังงานและสิ่งแวดล้อม มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี กรุงเทพ 10140

ชื่อวารสาร (อังกฤษ) Catalysis Communications

บทคัดย่อ (ไทย)

งานวิจัยนี้ศึกษาหาสภาวะที่เหมาะสมของกระบวนการไฮโดรเทอร์มอลคาร์บอไนเซชันที่อุณหภูมิ (180-250 องศาเซลเซียส) และเวลา (6-24 ชั่วโมง) เพื่อเตรียมคาร์บอนจากน้ำตาลกลูโคสซึ่งใช้เป็นตัวรองรับตัวเร่งปฏิกิริยาที่ใช้ในกระบวนการแปรสภาพน้ำตาลและเซลลูโลส จากการศึกษาพบว่า ไฮโดรเทอร์มอลคาร์บอนที่สภาวะต่าง ๆของการคาร์บอไนเซชันมีลักษณะทางเคมีและโครงสร้างเหมือนกัน ส่วนของเหลวที่ได้หลังผ่านไฮโดรเทอร์มอลคาร์บอไนเซชันสามารถบอกความเสถียรของไฮโดรเทอร์มอลคาร์บอนได้ โดยสภาวะที่เหมาะสมในการเตรียมคาร์บอนจากน้ำตาลกลูโคสให้มีความเสถียร คือ ไฮโดรเทอร์มอลคาร์บอไนเซชันที่อุณหภูมิ 220 องศาเซลเซียสเป็นเวลา 6 ชั่วโมง หลังจากนั้นนำคาร์บอนที่เตรียมจากสภาวะที่เหมาะสมไปผ่านกระบวนการซัลโฟเนชันเพื่อเตรียมตัวเร่งปฏิกิริยาคาร์บอนแบบกรด และทำการทดสอบตัวเร่งปฏิกิริยา จากการทดสอบพบว่าตัวเร่งปฏิกิริยาดังกล่าวมีความสามารถในการเร่งปฏิกิริยาไฮโดรไลซิสของเซลลูโลสและดีไฮเดรชันของน้ำตาลฟรุ๊กโตสได้ค่อนข้างสูง โดยให้ร้อยละผลได้ของน้ำตาลกลูโคส และ 5-ไฮดรอกซีเมทิลเฟอฟูรอล 43.63± 1.62 และ 20.29 ± 1.09 โดยมวล ตามลำดับ

เรื่องที่ 3

ชื่อเรื่อง (อังกฤษ) Sequential organosolv fractionation/hydrolysis of sugarcane bagasse: The coupling use of heterogeneous H_3PO_4-activated carbon as acid promoter and hydrolysis catalyst

ชื่อเรื่อง (ไทย) กระบวนการต่อเนื่องในการแยกองค์ประกอบทางเคมีโดยใช้ตัวทำละลายอินทรีย์และการย่อยของชานอ้อย: การใช้ถ่านกัมมันต์ที่ผ่านปฏิกิริยาการเติมกรดฟอสฟอริกเป็นตัวเร่งปฏิกิริยา ควบคู่ในกระบวนการแยกองค์ประกอบและการย่อยด้วยตัวเร่งปฏิกิริยา

ชื่อผู้เขียน (ไทย) นพรัตน์ สุริยะไชย[1], วีระวัตน์ แช่มปรีชา[2], จุฬารัตน์ ศักดารณรงค์[3], อาทิวรรณ โชติพฤกษ์[4] และนวดล เหล่าศิริพจน์[1]

ชื่อหน่วยงาน/สังกัดของผู้เขียน (ไทย)

1. บัณฑิตวิทยาลัยร่วมด้านพลังงานและสิ่งแวดล้อม มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี กรุงเทพ 10140
2. ห้องปฏิบัติการเทคโนโลยีเอนไซม์, ห้องปฏิบัติการพลังงานและเคมีชีวภาพ, ศูนย์พันธุวิศวกรรมและเทคโนโลยีชีวภาพแห่งชาติ, อุทยานวิทยาศาสตร์ประเทศไทย ปทุมธานี 12120
3. ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ มหาวิทยาลัยมหิดล นครปฐม 73170
4. ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย กรุงเทพ 10330

ชื่อวารสาร (อังกฤษ) Renewable Energy

บทคัดย่อ (ไทย)

การแยกองค์ประกอบของลิกโนเซลลูโลสและการย่อยสลายของส่วนที่เป็นโพลีแซคคาไรด์เป็นน้ำตาลซึ่งเป็นกระบวนการที่จำเป็นก่อนการผลิตเชื้อเพลิงชีวภาพและสารเคมี ในการศึกษานี้ได้ทำการศึกษากระบวนการต่อเนื่องในการแยกองค์ประกอบทางเคมีโดยใช้ตัวทำละลายอินทรีย์และการย่อยสลายในส่วนที่อุดมไปด้วยเซลลูโลสภายใต้น้ำร้อนที่ความดันสูง โดยใช้ถ่านกัมมันต์ที่ผ่านปฏิกิริยาการเติมกรดฟอสฟอริกเป็นตัวเร่งปฏิกิริยาซึ่งแสดงให้เห็นว่ามีประสิทธิภาพสูงด้านการคัดสรรค์ผลิตภัณฑ์และปริมาณผลผลิตในกระบวนการแยกองค์ประกอบซึ่งสัมพันธ์กับตัวเร่งปฏิกิริยาที่มีค่าพื้นที่ผิวและค่าความเป็นกรดที่สูง กระบวนการแยกองค์ประกอบใช้สารผสมตัวทำละลายอินทรีย์ที่ประกอบด้วย เมทิล ไอโซบิวทิล คีโตน/เมทานอล/น้ำ ในอัตราส่วน 16/68/16 โดยปริมาตร ที่อุณหภูมิ 180 องศสเซลเซียสเป็นเวลา 60 นาที โดยใช้ถ่านกัมมันต์ที่ผ่านปฏิกิริยาการเติมกรดฟอสฟอริกเป็นตัวเร่งปฏิกิริยา ทำให้ได้ของแข็งที่มีสัดส่วนของเซลลูโลสร้อยละ 88.9 รวมถึงการสลายของเฮมิเซลลูโลสไปเป็นน้ำตาลเพนโตสในชั้นน้ำเท่ากับร้อยละ 84.6 และ ปริมาณลิกนินที่ถูกสกัดไปในส่วนของชั้นตัวทำละลายเท่ากับร้อยละ 76.0 ซึ่งได้ทำการทดลองต่อเนื่องในส่วนของ

การย่อยภายใต้น้ำร้อนที่ความดันสูงโดยที่ไม่มีกระบวนการแยกของตัวเร่งปฏิกริยาที่อุณหภูมิ 225 องศาเซลเซียสเป็นเวลา 10 นาที พบว่าจากการย่อยได้ปริมาณน้ำตาลเฮกโซส เท่ากับร้อยละ 58.3 เมื่อเทียบกับอัตราส่วนเริ่มต้น หลังจากที่มีการนำตัวเร่งปฏิกิริยากลับมาใช้ใหม่อีก 5 ครั้งในกระบวนการ พบว่าประสิทธิภาพของตัวเร่งปฏิกิริยายังคงมากกว่าร้อยละ 80 ในงานวิจัยนี้แสดงให้เห็นถึงประสิทธิภาพในกระบวนการแยกองค์ประกอบและการย่อย โดยการใช้ตัวเร่งปฏิกิริยาที่เป็นกรด รวมถึงข้อดีของตัวเร่งปฏิกิริยาที่มีความสามารถสูงในการทำปฏิกิริยา การคัดสรรค์ผลิตภัณฑ์ และ สามารถนำตัวเร่งปฏิกิริยากลับมาใช้ใหม่

<u>เรื่องที่ 4</u>

ชื่อเรื่อง (อังกฤษ) The Effect of Pulsed Microwave Power on Transesterification of Chlorella sp. for Biodiesel Production

ชื่อเรื่อง (ไทย) ผลของพลังงานไมโครเวฟแบบพัลซ์ต่อปฏิการทรานเอสเทอร์ของคลอเรลลา สำหรับการผลิตไบโอดีเซล

ชื่อผู้เขียน (ไทย) ฉัตรทิพย์ พรหมหมวก[1], อิสระ ศิริวัฒนาวุฒิ[2], ประเสริฐ ภวสันต์[1], อาร์มานโด ที คิตาอิน[3], โมโตโนบุ โกโตะ[4] และอาทิวรรณ โชติพฤกษ์[1]

ชื่อหน่วยงาน/สังกัดของผู้เขียน (ไทย)

1. หน่วยปฏิบัติการวิศวกรรมเคมีเพื่อเพิ่มมูลค่าของทรัพยากรทางชีวภาพ ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย กรุงเทพ 10330
2. คณะวิศวกรรมศาสตร์ มหาวิทยาลัยกรุงเทพธนบุรี กรุงเทพ 10170
3. ภาควิชาชีวเคมีและเคมีประยุกต์ มหาวิทยาลัยกูมาโมโตะ ญี่ปุ่น
4. บัณฑิตวิทยาลัยด้านวิศวกรรม มหาวิทยาลัยนาโกยา ญี่ปุ่น

ชื่อวารสาร (อังกฤษ) Chemical Engineering Communications

บทคัดย่อ (ไทย)

พลังงานไมโครเวฟแบบพัลซ์สามารถใช้สำหรับการผลิตไบโอดีเซลจากคลอเรลลาด้วยปฏิกิริยาทรานส์เอสเทอริฟิเคชัน พลังงานไมโครเวฟและอุณหภูมิแบบเรียลไทม์ถูกนำมาใช้เพื่อประเมินประสิทธิภาพของการผลิตไบโอดีเซล โดยศึกษาการตั้งค่าพลังงานไมโครเวฟในช่วง 100-1000 วัตต์ เวลา (10 นาที) และอุณหภูมิ (60 องศาเซลเซียส) ในงานวิจัยนี้ที่ 250 วัตต์ ให้ปริมาณผลผลิตไบโอดีเซลต่อหน่วยพลังงานสูงสุด คือ ร้อย

ละ 0.53 โดยน้ำหนักของไขมันดิบต่อกิโลกรัมจูล จากผลการศึกษาพบว่าประสิทธิภาพในการผลิตไบโอดีเซลมีความสัมพันธ์กับความหนาแน่นและความถี่แบบพัลซ์ในระหว่างกระบวนการเกิดปฏิกิริยาที่ 250 วัตต์

เรื่องที่ 5

ชื่อเรื่อง (อังกฤษ) Hydrolysis of eucalyptus wood chips under hot compressed water in the presence of sulfonated carbon-based catalysts

ชื่อเรื่อง (ไทย) การทำไฮโดรไลซิสของเศษไม้ยูคาลิปตัสภายใต้น้ำร้อนอัดความดันโดยใช้ตัวเร่งปฏิกิริยาคาร์บอนซัลโฟเนต

ชื่อผู้เขียน (ไทย) ขัตติยะ วีระไสย[1], วีระวัตน์ แช่มปรีชา[2], จุพารัตน์ ศักดารณรงค์[3], อาทิวรรณ โชติพฤกษ์[4] และนวดล เหล่าศิริพจน์[1]

ชื่อหน่วยงาน/สังกัดของผู้เขียน (ไทย)

1. บัณฑิตวิทยาลัยร่วมด้านพลังงานและสิ่งแวดล้อม มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี กรุงเทพ 10140
2. ห้องปฏิบัติการเทคโนโลยีเอนไซม์, ห้องปฏิบัติการพลังงานและเคมีชีวภาพ, ศูนย์พันธุวิศวกรรมและเทคโนโลยีชีวภาพแห่งชาติ, อุทยานวิทยาศาสตร์ประเทศไทย ปทุมธานี 12120
3. ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ มหาวิทยาลัยมหิดล นครปฐม 73170
4. ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย กรุงเทพ 10330

ชื่อวารสาร (อังกฤษ) Food and Bioproducts Processing

บทคัดย่อ (ไทย)

การไฮโดรไลซิสเป็นกระบวนการสำคัญในการย่อยสลายของลิกโนเซลลูโลส หรือชีวมวล เพื่อผลิตน้ำตาลและสารอนุพันธ์ ซึ่งใช้ในกระบวนการผลิตเชื้อเพลิงชีวภาพและสารเคมีสินค้าโภคภัณฑ์ งานวิจัยนี้ทำการศึกษากระบวนการไฮโดรไลซิสของยูคาลิปตัสโดยใช้ตัวเร่งปฏิกิริยาคาร์บอนซัลโฟเนตที่เตรียมคาร์บอนจากน้ำตาล 3 ชนิด (น้ำตาลซูโครส น้ำตาลกลูโคส และ น้ำตาลไซโลส) ด้วยน้ำร้อนอัดความดันที่อุณหภูมิ 150-250 องศาเซลเซียส เป็นเวลา 1-10 นาที จากการศึกษาพบว่าการเพิ่มอุณหภูมิน้ำร้อนอัดความดันถึง 200 องศาเซลเซียสจะทำให้ร้อยละผลได้น้ำตาลจากเซลลูโลสและเฮมิเซลลูโลสสูงขึ้น ในขณะที่อุณหภูมิมากกว่า 200 องศาเซลเซียสส่งผลให้น้ำตาลเกิดการเสื่อมสภาพ เมื่อเปรียบเทียบประสิทธิภาพของตัวเร่งปฏิกิริยา พบว่า ตัวเร่งปฏิกิริยาที่เตรียมจากน้ำตาลซูโครสมีประสิทธิภาพในการผลิตน้ำตาลมากที่สุด เนื่องจากมีค่าความเป็นกรดสูง ซึ่งสภาวะในการไฮโดรลิสยูคาลิปตัสที่ให้ร้อยละผลได้น้ำตาล (ผลรวมน้ำตาล

กลูโคส น้ำตาลฟลุ๊กโตส และน้ำตาลไซโลส) สูงที่สุดร้อยละ 40.7 คือ การใช้ตัวเร่งปฏิกิริยาที่เตรียมจากน้ำตาลซูโครสปริมาณร้อยละ 5 โดยมวล ที่อุณหภูมิ 200 องศาเซลเซียส เป็นเวลา 5 นาที โดยใช้ยูคาลิปตัสที่ผ่านการบดให้มีขนาด 60-100 ไมโครเมตร และปรับสภาพโดยใช้กระบวนการออกซิเดชั่นด้วยด่าง ซึ่งงานวิจัยนี้เป็นการผลิตตัวเร่งปฏิกิริยาทางเลือกสำหรับการย่อยสลายของลิกโนเซลลูโลส ในอุตสาหกรรมชีวมวล

<u>เรื่องที่ 6</u>

ชื่อเรื่อง (อังกฤษ) Enhanced Levulinic Acid Production from Cellulose by Combined Brønsted Hydrothermal Carbon and Lewis Acid Catalysts

ชื่อเรื่อง (ไทย) การปรับสภาพของรำข้าวที่สกัดน้ำมันออกแล้วเพื่อการเพิ่มปริมาณสารประกอบฟินอลิครวมด้วยการสกัดด้วยน้ำกึ่งวิกฤต

ชื่อผู้เขียน (ไทย) ธรรศ บุญญกาญจน์[1], ปิยาภรณ์ วทานิยะกุล[1], ปณัฐพงศ์ บุญนวล[2], อาร์มานโด ที คิตาอิน[3], เทสสึยะ คิดะ[3], มิตซูรุ ซาซากิ[3], นวดล เหล่าศิริพจน์[4], บรรเจิด จูงสมจิตร์[1] และอาทิวรรณ โชติพฤกษ์[1]

ชื่อหน่วยงาน/สังกัดของผู้เขียน (ไทย)

1. หน่วยปฏิบัติการวิศวกรรมเคมีเพื่อเพิ่มมูลค่าของทรัพยากรทางชีวภาพ ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย กรุงเทพ 10330
2. ภาควิชาวิศวกรรมอุตสาหการ คณะวิศวกรรมศาสตร์ มหาวิทยาลัยนเรศวร พิษณุโลก 65000
3. ภาควิชาชีวเคมีและเคมีประยุกต์ มหาวิทยาลัยคุมาโมโตะ ญี่ปุ่น
4. บัณฑิตวิทยาลัยร่วมด้านพลังงานและสิ่งแวดล้อม มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี กรุงเทพ 10140

ชื่อวารสาร (อังกฤษ) Applied Catalysis A: General

บทคัดย่อ (ไทย)

การศึกษานี้แสดงให้เห็นระบบของการเร่งปฏิกิริยาด้วยการใช้ตัวเร่งปฏิกิริยาไฮโดรเทอมอลคาร์บอนแบบกรดร่วมกับกรดลิวอิส ซึ่งเป็นการทำงานร่วมกันแบบเสริมกันเพื่อเพิ่มประสิทธิในการผลิตกรดเลวูนิลิกจากเซลลูโลส ขั้นตอนแรกทำการเตรียมตัวเร่งปฏิกิริยาไฮโดรเทอมอลคาร์บอนแบบกรดด้วยกระบวนการบวนการไฮโดรเทอมอลคาร์บอไนเซชันและการติดหมู่ฟังก์ชันด้วยกรดซัลฟูริก จากนั้นทำการศึกษากรดลิวอิสได้แก่ แมงกานีสคลอไรด์ ไอเอิร์นคลอไรด์ โคบอลต์คลอไรด์ แคดเมียมคลอไรด์ และ โครเมียมคลอไรด์ ซึ่งพบว่าโครเมียมคลอไรด์ ให้ร้อยละผลได้ของกรดเลวูลินิก มากที่สุด ดังนั้นโครเมียมคลอไรด์จึงถูกเลือกเพื่อ

ใช้ร่วมกับตัวเร่งปฏิกิริยาไฮโดรเทอมอลคาร์บอนแบบกรดในการผลิตกรดเลวูนิลิกจากเซลลูโลส ซึ่งสภาวะที่เหมาะสมสำหรับการใช้ตัวเร่งปฏิกิริยาทั้งสองร่วมกันคือ การใช้ปริมาณตัวเร่งปฏิกิริยาไฮโดรเทอร์มอลคาร์บอนแบบกรดร้อยละ 5 โดยมวล ความเข้มข้นของโครเมียมคลอไรด์ 0.015 โมลาร์ อุณหภูมิ 200 องศาเซลเซียส และเวลา 5 นาที ที่สภาวะดังกล่าวนี้สามารถเพิ่มร้อยละผลได้ของกรดเลวูลินิกสูงถึง 40 โดยมวล ซึ่งเปรียบเทียบกับการใช้โครเมียมคลอไรด์เพียงอย่างเดียวให้ร้อยละผลได้ของกรดเลวูลินิก 30โดยมวล

สรุปงานวิจัย

จากผลการวิจัยพบว่าตัวเร่งปฏิกิริยาวิวิธพันธ์จำพวกคาร์บอนที่เตรียมจากน้ำตาลกลูโคสและรำข้าวสกัดน้ำมัน มีความเป็นกรดและมีความเสถียรทางความร้อนสูง ทั้งนี้ตัวเร่งปฏิกิริยาดังกล่าวยังมีความสามารถในการเร่งปฏิกิริยาของการแปรสภาพชีวมวลเป็นสารเคมีที่มีมูลค่าสูง และการผลิตไบโอดีเซล ซึ่งนำไปสู่การประยุกต์ใช้ในปฏิกิริยาอื่นๆ ที่ต้องใช้ตัวเร่งปฏิกิริยาชนิดกรด ดังนั้นงานวิจัยนี้มีประโยชน์ทั้งการพัฒนาตัวเร่งปฏิกิริยาจากวัตถุที่มีราคาถูก และการเพิ่มประสิทธิภาพของการผลิตสารที่มีมูลค่าด้วยตัวเร่งปฏิกิริยาดังกล่าว อย่างไรก็ตามเมื่อเปลี่ยนสารตั้งต้นในการสังเคราะห์ตัวเร่งปฏิกิริยาจำพวกคาร์บอนแบบกรด จำเป็นต้องมีการศึกษาหาสภาวะที่เหมาะสมในการเตรียมตัวเร่งปฏิกิริยานั้น

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Preparation of hydrothermal carbon acid catalyst from defatted rice bran

Piyaporn Wataniyakul[a], Panatpong Boonnoun[b], Armando T. Quitain[c], Tetsuya Kida[c], Navadol Laosiripojana[d], Artiwan Shotipruk[a,*]

[a] Chemical Engineering Research Unit for Value Adding of Bioresources, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Phayathai Road, Bangkok 10330, Thailand
[b] Department of Industrial Engineering, Chemical Engineering program, Faculty of Engineering, Naresuan University, Phitsanulok 65000, Thailand
[c] Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860-8555, Japan
[d] The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Prachauthit Road, Bangmod, Bangkok 10140, Thailand

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ABSTRACT

In this study, the effects of carbonization conditions: temperature (180–250 °C) and time (1–8 h) on the yield and the chemical characteristics of hydrothermal carbon derived from defatted rice bran (HTCDRB) were determined. The morphological and chemical characteristics of the sulfonated HTCDRB catalyst were also examined. In addition, the stability of the catalyst was evaluated based on the amounts of biomass conversion products (5-hydroxymethylfurfural (HMF), furfural, levulinic acid and formic acid) leached into water at a specified biomass conversion condition. Since no HMF and furfural, and only small amounts of levulinic acid (1.75 wt.%), and formic acid (0.42 wt.%), were leached from the catalyst synthesized from HTCDRB prepared at the carbonization condition of 220 °C for 3 h, this condition was suggested to be a suitable carbonization condition. Despite having similar structural and chemical characteristics, the leaching test suggested that the DRB-based hydrothermal carbon catalyst was found to be more stable than the glucose-based hydrothermal carbon catalyst, prepared at the same condition. The catalytic activity for cellulose hydrolysis of the catalyst was higher than that of the commercial Amberlyst 16 WET catalyst.

1. Introduction

Owing to the increased world population, the rising energy demand for transportation and industries to produce various consumer products has inevitably become an important societal issue. Consequently, research on development of technology for effective processing and utilization of non-petroleum feedstocks for production of biomaterials, fine chemicals and alternative fuels has now been under attention globally. Taking rice, the major food crop of Asian countries including Thailand, as an example, other than the edible milled rice, all other parts of rice are being extensively researched to provide the maximal benefits to human. Rice straws and rice husks are generally burned to produce heat (Kataki et al., 2017; Quispe et al., 2017). More recent research has been focusing on their conversion into other high energy-density fuels and valuable chemicals such as production of ethanol, methane, acetic acid, sugar (glucose and xylose), 5-hydroxymethylfurfural (HMF), and furfural (Das et al., 2013; de Assis Castro et al., 2016). Given its high silica content, rice husks have been processed in silica synthesis, amine-modified SiO_2 aerogel preparation, synthesis of belite cement, and development of refractory ceramics materials (Sinyoung et al., 2017; Sobrosa et al., 2017). Rice bran, due to the high oil content, is extracted for edible oil (Capellini et al., 2017; Lakkakula et al., 2004; Mamidipally and Liu, 2004). Defatted rice bran (DRB), the residue from the rice bran oil industry, have been researched for extraction of protein (Bandyopadhyay et al., 2012; Jongjareonrak et al., 2015) and phenolic compounds (Chiou et al., 2012; Devi and Arumughan, 2007; Wataniyakul et al., 2012) through various processes ranging from enzymatic extraction/hydrolysis to subcritical water extraction/hydrolysis by a number of research groups (Hata et al., 2008; Sereewatthanawut et al., 2008; Sunphorka et al., 2012; Viriya-Empikul et al., 2012).

In most industrial processes including those of bio-based nature, catalysts have for a long time played a key role. Research studies are being conducted to develop heterogeneous catalysts to replace the conventionally used homogeneous catalysts, due to their ease of separation and reusability. Owing to the low cost of raw materials, carbon-based acid catalyst, has recently been developed from various carbon sources such as sugars, polycyclic aromatic compounds,

* Corresponding author at: Chemical Engineering Research Unit for Value Adding of Bioresources, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Phayathai Road, Bangkok, 10330, Thailand.
E-mail address: Artiwan.Sh@chula.ac.th (A. Shotipruk).

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polystyrene resins, activated biochar, and lignin (Mo et al., 2008; Toda et al., 2005; Yao et al., 2017; Yu et al., 2010), and have been applied to processes involving biofuel and biochemical production. Such catalysts can be produced via rather simple synthesis route, either by carbonization of sulfopolycyclic aromatic carbons or sulfonation of carbonized inorganic/organic compounds (Boonnoun et al., 2010; Gao et al., 2007; Shu et al., 2009). Other advantages of this class of catalyst include high acid density and high thermal stability. Carbon-based solid catalysts synthesized from various carbon sources such as glucose and biomass have been tested for the production of biodiesel by esterification and transesterification (Han et al., 2016; Yu et al., 2010) and biomass conversion via processes in hot compressed water, particularly, hydrolysis of biomass to monomer sugars, and dehydration of the monomer sugars to furan compounds such as HMF and furfural (Daengprasert et al., 2011; Li et al., 2015). These furan compounds are, not only the key intermediates for liquid fuels, but also important platform chemicals for production of various chemicals and polymers.

Although various types of carbon sources such as glucose (Zong et al., 2007) and cellulose (Suganuma et al., 2010) can be used for the preparation of carbon-based catalysts, the biomass derived carbon source offers additional advantages of being renewable and being available in abundance at extremely low cost. When biomass is used, the first few catalyst synthesis steps resemble those of the activated carbon preparation. These involve water removal (dehydration) and conversion of organic matter to elemental carbon by driving off the non-carbon portion with heat (carbonization), and optionally, followed by pore enlargement (activation). To further make the carbon more suitable for catalysing a specified reaction, the surface chemical properties of the carbon may be modified by means of physical or chemical functionalization. Nevertheless, a major bottleneck of this preparation process is the use of high carbonization/pyrolysis temperatures (400–800 °C) (Jindo et al., 2014). The energy requirement becomes even more consuming, particularly when additional heat is needed to remove water from biomass with high moisture content.

A new method for preparation of carbonaceous materials has recently been developed, in which carbonization of the carbon sources takes place in hot compressed water at moderate temperature (180–250 °C) under self-generated pressure (Fiori et al., 2014; Libra et al., 2011). This process results in hydrothermal carbon (HTC) that could be further functionalized to perform specific catalytic activity. It should be noted that, the hydrothermal carbonization process resembles that of biomass conversion to produce HMF, furfural, and other valuable products such as glucose, levulinic acid, and formic acid. The main difference is that the HTC production from biomass requires much longer time from one to several hours (Libra et al., 2011). For this reason, biomass residues (i.e. DRB) that have been extracted for high value products (amino acids (Sereewatthanawut et al., 2008), phenolic compounds (Wataniyakul et al., 2012), and etc.), could potentially be a very attractive carbon source for HTC production.

This study therefore aims to investigate the possibility for synthesizing a HTC from DRB, with a specific objective to understand the effect of hydrothermal conditions on the characteristics of DRB derived HTC. The thermal stability of the catalyst obtained by functionalization of the HTC with sulfuric acid, a strong acid commonly used for carbon-based acid catalyst preparation, was also evaluated based on the Thermogravimetric Analyzer (TGA) results. Furthermore, the catalytic activity of the HTC catalyst on cellulose hydrolysis was investigated. In addition, if the catalyst is to be used in biomass conversion, due to the similar chemical nature of the carbon catalyst and the starting biomass, the stability of the prepared catalyst should also be evaluated based on the leaching of biomass conversion products (i.e. HMF, furfural, levulinic acid and formic acid) from the catalyst itself at a specified biomass conversion condition.

2. Materials and methods

2.1. Materials

Defatted rice bran used in this study was obtained from Thai Edible Oil Co., Ltd., Thailand. The chemical compositions (percent lignin, cellulose, hemicelluloses, and ash) of defatted rice bran were analysed using the standard NREL's method (Sluiter et al., 2008). The defatted rice bran was found to comprise of cellulose (25.48 wt.%), hemicellulose (9.35 wt.%), lignin (25.63 wt.%), ash (9.89 wt.%), and others (29.65 wt.%). D-Glucose anhydrous was of analytical grade and was purchased from Ajax Finechem Pty Ltd (Thailand). Sulfuric acid was of analytical grade and was purchased from Fluka (Singapore). Cellulose powdered, HMF, furfural, levulinic acid, formic acid, and perchloric acid ($HClO_4$) were of analytical grade and were purchased from Wako Pure Chemical Company (Osaka, Japan). The commercial grade sulfonated solid catalyst-Amberlyst 16 WET was purchased from Fluka (Singapore).

2.2. Preparation of hydrothermal carbon

The HTC was prepared in an 8.8 ml SUS-316 stainless steel closed batch reactor (AKICO Co., Japan) by hydrothermally carbonizing 1 g of carbon materials (DRB or glucose) in 5 ml of deionized water. The closed batch reactor containing water and the carbon source was heated with an electric heater to the desired temperature, 180–250 °C. This generally took approximately 15–25 min depending on the setpoint temperature. After a holding period of 1–8 h at the desired reaction temperature, the reactor was cooled to room temperature by submerging it into a water bath. The resulting solid HTC was separated from the liquid carbonization portion by a filter paper (Whatman no.1), and it was then washed with deionized water until the pH of the washed water was neutral. After drying overnight at 110 °C, the resulted HTC was stored in a sealed plastic bag for further analysis. The DRB and glucose derived HTC are called HTCDRB and HTCG, respectively.

2.3. Preparation of sulfonated hydrothermal carbon-based catalyst

The HTC-based catalyst (HTC-SO_3H) was prepared by sulfonation of the HTC following the method described by Yu et al. (2010). Briefly, 5 g of HTC was heated in 50 ml of concentrated H_2SO_4 (> 96%) using a 3-neck round bottom flask at 150 °C for 15 h under N_2 flow. The condenser was connected to 3-neck round bottom flask to condense the acid vapor. A 1-l flask containing activated carbon was connected to the condenser to trap the condensed acid. The remaining acid vapor was then trapped by water in another 1-l flask connected to the system. The obtained solid acid catalyst was washed with deionized water (1000 ml) before being separated with a vacuum filter. The solid was repeatedly washed with boiling distilled water until no change in water pH was observed. After drying overnight at 110 °C, the HTC-SO_3H catalyst was obtained. The DRB and glucose derived HTC-based catalysts are called HTCDRB-SO_3H and HTCG-SO_3H, respectively.

2.4. Analysis and characterizations

The HTC yield was determined as the percentage of weight ratio (dry basis) of the produced HTC and raw materials (DRB and glucose). The elemental compositions (C, H, and N) of raw material and HTC samples were determined by a CHN analyzer (LECO CHN628 elemental analyzer). The sulphur content (S) of samples was determined by a TruSpec Sulphur (LECO Corporation, USA). The oxygen (O) was calculated by subtraction of C, H, N, and S content from 100%. Furthermore, the surface morphologies of HTC were observed by Field Emission Scanning Electron Microscopy (FESEM) using a FEI Quanta 200 microscope (Eindhoven, Netherlands) operated at 2 kV.

The structural analysis of HTC and HTC-SO_3H was examined by X-

ray diffraction (XRD) performed using RINT 2100 diffractometer, RIGAGU. Each sample was scanned in the range of 2–60 °. Fourier transform infrared spectroscopy (FTIR) was obtained using a Jasco FT-IR-4100 spectrometer to characterize the functional groups of the samples. Prior to each measurement, the sample was ground into fine particles and mixed with KBr to prepare disks. The spectrum was recorded in wavenumber from 4000 to 500 cm^{-1} with resolution of 4 cm^{-1}. The thermal stability of each sample was determined by Thermogravimetric Analyzer (TGA) using a TG/DTA6200 Thermogravimetric analyzer. Non-isothermal combustion of HTCs was conducted in the furnace of the TGA system under a nitrogen gas atmosphere at flow rate of 10 ml/min and heating rate of 10 °C/min from 45 °C to 500 °C. The sample weight was continuously recorded under the experimental conditions. The specific area, pore volume and pore size diameter of the samples were determined by N_2 physisorption technique using the Brunauer-Emmet-Teller (BET) method with a Belsorp-mini (BEL Japan, Tokyo, Japan); the samples were pretreated to remove moisture at 150 °C for 3 h prior to measurement. The total sample acidities and the sulfonic (-SO_3H) groups concentrations were measured by neutralization titration method (Wu et al., 2010). The HTCDRB and HTCG are labeled as HTCDRBX-Y and HTCGX-Y, respectively, where X (X = 180, 220, 250 °C) is the hydrothermal carbonization temperature, Y (Y = 1, 3, 8 h) is the hydrothermal carbonization time. The HTCDRB-SO_3H and HTCG-SO_3H are labeled as HTCDRBX-Y-SO_3H and HTCGX-Y-SO_3H, respectively.

2.5. Catalyst leaching test under microwave-assisted hydrothermal reaction condition

Microwave heating offers the advantage of shorter required treatment times, accompanied by a consequent reduction in energy consumption. It was therefore used as a mean to provide accelerated biomass conversion condition for the evaluation of the leaching of chemicals from the synthesized HTC-SO_3H catalyst. For each batch of microwave treatment experiment, approximate 0.05 g of catalyst and 5 ml of deionized water were charged into a 100 ml polyetheretherketone (PEEK) vessel. The vessel was then closed and placed in the microwave field. Microwave irradiation at 300 W was turned on until the temperature of the vessel content reached 200 °C (approximately 12 min) and was maintained at this temperature for the next 5 min. After allowing the system to cool down (taking approximately 20 min), the liquid and the solid catalyst were removed from the vessel and were separated using a filter paper. The solid residue was washed with 5 ml deionized water, while the liquid was assayed for the amounts of HMF, furfural, levulinic acid, and formic acid.

The concentrations of HMF, furfural, levulinic acid, and formic acid in the liquid fraction were quantified in accordance with the methods described by Mission et al. (2017), using a high performance liquid chromatography (HPLC, JASCO International Co., Ltd., Japan), equipped with a Jasco PU980 pump, a Shodex SUGAR SH1011 (8.0mmID*300 mm), a Sugai U-620 column heater, a Jasco AS-2055 plus automated sampler injector and a Jasco UV-970 detector. The column temperature was set at 60 °C and the injection volume was set at 10 µl, and 0.3 mM $HClO_4$ was used as an eluent at a flow rate of 0.5 ml/min. The UV absorbance was measured at 220 nm. The retention times of HMF, furfural, levulinic acid, and formic acid were found to be 39.4, 57.0, 23.3 and 21.2 min, respectively. The amounts of the leached components from the catalyst were reported as mass percentages of the starting material (DRB or glucose).

2.6. Catalytic activity test on cellulose hydrolysis

The HTC-SO_3H was tested toward the cellulose hydrolysis. It is noted that the commercial grade sulfonated solid catalyst-Amberlyst 16 WET was also tested for comparison. The reaction was carried out in an 8.8 ml SUS-316 stainless steel closed batch reactor (Suan Luang Engineering Ltd., Part.), into which 0.1 g of cellulose, 5 ml of deionized water, and 0.005 g of catalyst were charged. The reactor was shaken and heated to the desired reaction temperature (180 °C) by an electric heater connected to a temperature controller, and was maintained at this temperature for 5 min. After the reaction, the reactor was quenched in a water bath at room temperature. Subsequently, the solid and the liquid reaction products were removed from the reactor, and they were separated by filtration through a Whatman No. 1 filter paper. The liquid products were then determined for the amounts of glucose, HMF and furfural.

The quantification and identification of glucose in the liquid products was conducted using an HPLC equipped with an evaporative light scattering detector (ELSD) detector with a Rezex RPM Monosaccharide Pb + 2 (7.8mmID*300) column. The column temperature was set at 60 °C. Injection volume was set at 5 µl and water was used as the eluent at a flow rate of 0.6 ml/min. The retention time of glucose was 13.3 min. The HPLC analyses for the amounts of HMF and furfural were carried out using a Varian C18 (4.6mmID*250) column at 25 °C, with 90% (1% aq. Acetic acid):10% methanol used as the eluent. The eluent flow rate was 1 ml/min, and the injection volume was set at 5 µl. The concentrations of HMF and furfural were measured based on UV absorbance at 285 nm. The retention times of HMF and furfural were 6.6 min and 9.0 min, respectively. The yields of the reaction products: glucose, HMF and furfural were calculated as mass percentages of the starting cellulose.

3. Results and discussion

3.1. Yield and characteristics of hydrothermal carbon

The HTC yields obtained by hydrothermal carbonization of DRB and glucose are shown in Table 1. Similar to the results reported in previous studies (Hoekman et al., 2011; Kim et al., 2015), the yield of HTCDRB was found to decrease with increasing carbonization temperature. For carbonization time, the HTCDRB yield stayed relatively constant as residence time increased from 1 to 3 h, but significantly decreased when the residence time increased from 3 to 8 h at all carbonization temperatures. The HTCDRB yield decreased with increasing temperature and time, probably due to the hydrolysis and the decomposition of the components such as cellulose, hemicellulose, and lignin in DRB. As the carbonization temperature increased, the heated water, typically under subcritical condition, enhanced the dissolution of organic components of the biomass, as well as increased the extent of biomass gasification (Falco et al., 2011; Gao et al., 2016), resulting in the drop in HTCDRB yield. The effects of hydrothermal carbonization temperature and time on the yield of HTCG, on the other hand, showed a reversed direction. The yield of HTCG increased with the increase in both temperature and residence time. Particularly, at low temperature of 180 °C, significant increase in HTCG yield was observed with increased residence time.

Morphological structures of HTCDRB and HTCG, as shown in Fig. 1 and Fig. 2, respectively, were completely different. The HTCDRB was found to have highly complex structures, while on the other hand, HTCG was spherical, and had smooth surfaces. As shown in Fig. 2, the spherical particles were of various sizes between 0.5–10 µm, and appeared to agglomerate. These findings are similar to those of Nata and Lee (2010) and Titirici et al. (2012). It was also evident that the size of the HTCG became larger as the hydrothermal carbonization temperature and time increased, possibly due to the growth of the individual particles as well as the increase in agglomeration of the particles over time.

The time dependence on HTC yield (see Table 1) and morphological structures of the HTCDRB and HTCG (Figs. 1 and 2) suggested that the HTC formation from DRB and glucose took different routes. Starting with glucose solution, the HTC formation would involve dehydration of glucose to HMF, polymerization and aromatization of HMF to aromatic

Table 1
HTC yields and elemental compositions of carbonaceous materials before and after hydrothermal carbonization.

Sample name	Elemental compositions (wt.%)					Atomic ratio			HTC yield (wt.%)
	C	H	O	N	S	H/C	O/C	Chemical composition	
DRB	38.44	7.36	50.93	2.55	0.73	0.19	1.32	$CH_{0.191}O_{1.325}N_{0.066}S_{0.019}$	–
HTCDRB180-1	55.65	13.36	28.12	2.10	0.77	0.24	0.51	$CH_{0.240}O_{0.505}$ $N_{0.038}S_{0.014}$	40.06
HTCDRB180-3	65.54	14.16	18.74	0.98	0.58	0.22	0.29	$CH_{0.216}O_{0.286}$ $N_{0.015}S_{0.009}$	40.92
HTCDRB180-8	62.44	15.13	21.88	0.00	0.55	0.24	0.35	$CH_{0.242}O_{0.350}$ $S_{0.009}$	29.95
HTCDRB220-1	69.67	13.61	15.30	0.88	0.54	0.20	0.22	$CH_{0.195}O_{0.220}$ $N_{0.013}S_{0.008}$	38.40
HTCDRB220-3	73.44	15.28	11.75	0.00	0.53	0.21	0.15	$CH_{0.208}O_{0.146}S_{0.007}$	38.77
HTCDRB220-8	72.23	14.30	12.43	0.53	0.51	0.20	0.17	$CH_{0.198}O_{0.172}$ $N_{0.007}S_{0.007}$	26.91
HTCDRB250-1	73.14	14.25	11.68	0.44	0.49	0.19	0.16	$CH_{0.195}O_{0.160}$ $N_{0.006}S_{0.007}$	33.68
HTCDRB250-3	75.49	12.74	9.77	1.53	0.47	0.17	0.13	$CH_{0.169}O_{0.129}$ $N_{0.020}S_{0.006}$	32.03
HTCDRB250-8	70.91	9.30	16.58	2.70	0.51	0.13	0.23	$CH_{0.131}O_{0.234}$ $N_{0.038}S_{0.007}$	24.04
Glucose	39.10	8.07	52.83	0.00	0.00	0.21	1.35	$CH_{0.206}O_{1.351}$	–
HTCG180-1	64.56	13.09	22.35	0.00	0.00	0.20	0.35	$CH_{0.203}O_{0.346}$	3.25
HTCG180-3	62.34	7.65	30.01	0.00	0.00	0.12	0.48	$CH_{0.123}O_{0.418}$	12.74
HTCG180-8	61.90	7.04	31.06	0.00	0.00	0.11	0.50	$CH_{0.124}O_{0.502}$	23.90
HTCG220-1	66.28	8.90	24.82	0.00	0.00	0.13	0.37	$CH_{0.134}O_{0.374}$	29.45
HTCG220-3	69.29	9.38	21.33	0.00	0.00	0.14	0.31	$CH_{0.135}O_{0.308}$	37.42
HTCG220-8	70.08	10.31	19.61	0.00	0.00	0.15	0.28	$CH_{0.147}O_{0.280}$	39.84
HTCG250-1	68.41	7.30	24.09	0.00	0.00	0.11	0.36	$CH_{0.107}O_{0.355}$	36.76
HTCG250-3	72.74	10.21	17.05	0.00	0.00	0.14	0.23	$CH_{0.140}O_{0.234}$	39.03
HTCG250-8	71.22	9.53	19.25	0.00	0.00	0.13	0.27	$CH_{0.134}O_{0.270}$	41.12

unit, and condensation of aromatic unit to aromatic carbon called hydrothermal carbon (Baccile et al., 2009). While HTC formation from DRB might take the same route with an additional DRB hydrolysis step, HTCDRB could also be formed directly from DRB via melting, condensation, and decarboxylation. Apparent from the decrease in HTC yield with time and the HTCDRB morphologies, it was suggested that the direct route of HTC formation would be more prominent when starting from complex biomass such as DRB.

The elemental compositions of carbonaceous materials: DRB and glucose before and after hydrothermal carbonization are summarized in Table 1. It can be seen from this table that, for DRB, the percentage of carbon considerably increased after hydrothermal carbonization. The percentage of carbon was also found to increase with increasing carbonization time from 1 to 3 h, and stayed relatively constant onwards at all temperatures. For glucose, similar trend was observed, particularly at temperature of 220 and 250 °C. At the carbonization temperature of 180 °C, on the other hand, the percentages of carbon were relatively low (62–64%) and remained rather constant with increasing residence times, suggesting that the temperature of 180 °C might not be sufficient for carbonization of the carbon substrates. The hydrothermal carbonization condition that gave the highest carbon content for both DRB and glucose was 3 h and 250 °C, resulting in 75 wt.% and 72 wt.% carbon,

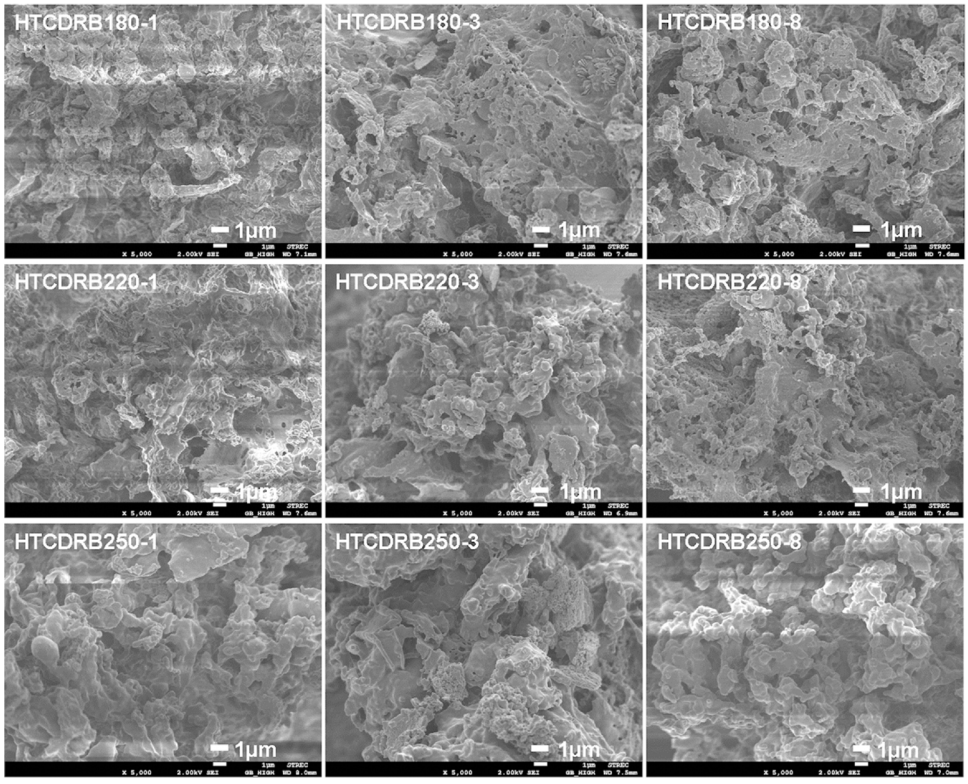

Fig. 1. SEM images of DRB derived carbons by hydrothermal carbonization at various temperatures and times.

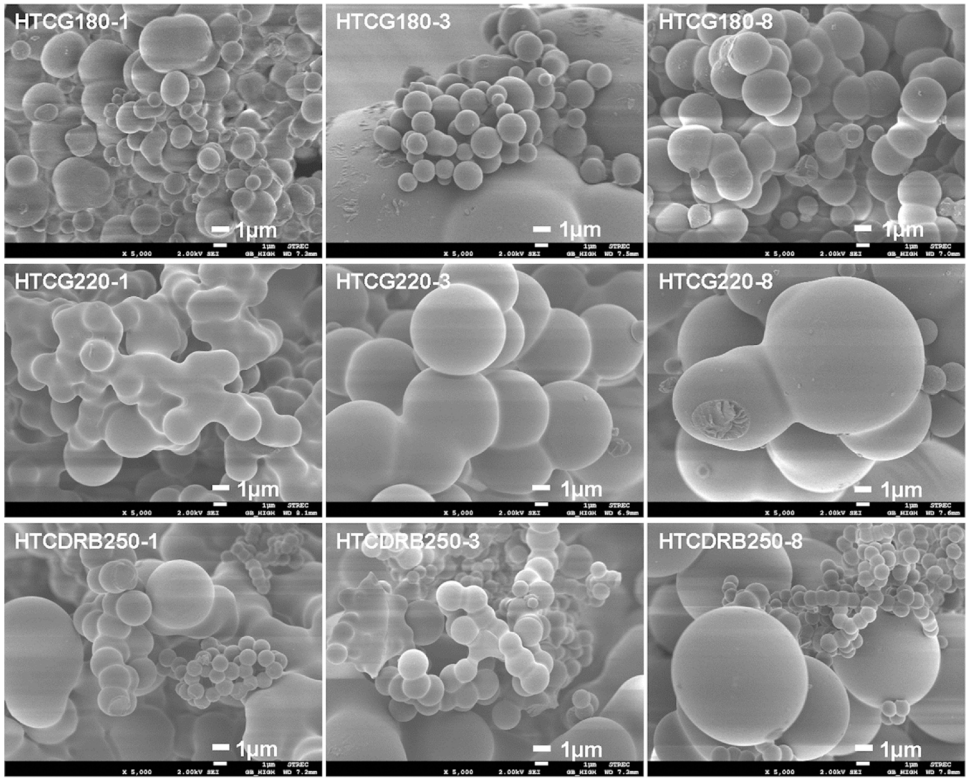

Fig. 2. SEM images of glucose derived carbons by hydrothermal carbonization at various temperatures and times.

respectively. Moreover, the H/C and O/C atomic ratios were also analysed. For HTCDRB, an increase in the hydrothermal carbonization temperature from 180 to 250 °C caused a decrease in the H/C and O/C atomic ratios (**see** Table 1), suggesting an increase in the degree of condensation as temperature increased. The effect of temperature was much higher than that of the reaction time. For instance, at 220 °C, an increase in reaction time from 1 to 8 h did not lead to the decrease in those atomic ratios. For glucose, the ratio of O/C decreased at greater extent than the H/C ratio when the temperature increased from 180 to 220 °C, indicating that decarboxylation reactions were more relevant in the elemental transformation than dehydration. Particularly, the observed values of O/C below 0.4 indicated that dehydration was nearly completed and the decarboxylation became more prominent (Röhrdanz et al., 2016). Both HTCDRB and HTCG at the hydrothermal carbonization temperature of 220 and 250 °C had the O/C atomic ratios below 0.4 for all residence times. The carbon contents in all HTCDRB and HTCG, prepared at both temperatures, however were not significantly different. Therefore, the HTCs formed at the hydrothermal carbonization conditions of 220 °C for 1 and 3 h were selected for further use as an acid catalyst support for biomass conversion.

3.2. Characteristics of sulfonated hydrothermal carbon-based catalysts

The selected HTC derived from DRB and glucose were sulfonated with concentrated sulfuric acid to prepare HTC-SO_3H. The characteristics of HTC and the corresponding HTC-SO_3H were compared base on XRD, FTIR and TGA measurements as shown in Figs. 3–5. The XRD patterns of the selected HTCDRB show amorphous carbon structure, suggesting that it is composed of aromatic carbon sheets oriented in a considerably random fashion at broad diffraction peak (2θ = 10°–30°) (Fig. 3(a)). After sulfonation, beside the broad diffraction peak (2θ = 10°–30°), a diffraction peak (2θ = 35°–50°) was also seen in HTCDRB-SO_3H (Fig. 3(b)). It is noted that the XRD patterns were similar to those of previous studies (Okamura et al., 2006; Suganuma et al., 2008). The results indicated that further carbonization occurred during sulfonation, resulting in HTCDRB-SO_3H with larger carbon sheet than that of HTCDRB. It should also be noted that HTCG and HTCG-SO_3H have similar XRD patterns to those of HTCDRB and HTCDRB-SO_3H, respectively.

The FTIR spectra of HTC and the corresponding HTC-SO_3H are shown in Fig. 4(a) and (b), respectively. The results indicated that the functional groups of HTCDRB were similar to HTCG, and those of HTCDRB-SO_3H and HTCG-SO_3H were also similar. The presence of aromatic components was evidenced by the aromatic C—H out-of-plane bending vibrations at bands in the 875–750 cm^{-1} region, and the C=C vibrations band approximately at 1600 cm^{-1}. Moreover, the presence of oxygen groups was suggested by the bands at 3700–3000 cm^{-1} (a wide band attributed to O—H stretching vibration in hydroxyl or carboxyl groups), 1710 cm^{-1} (C=O vibrations corresponding to carbonyl, quinone, ester or carboxyl), and 1460–1000 cm^{-1} (C—O stretching vibration in hydroxyl, ester or ether and O—H bending vibrations) (Fu et al., 2013; Sevilla and Fuertes, 2009). For HTC, the presence of a peak appearing at approximately 3000–2815 cm^{-1} was attributed to stretching vibrations of aliphatic C—H, indicating that carbonization might have not been completed. After sulfonation, the aliphatic group however no longer appeared (Fraile et al., 2012), possibly because further carbonization occurred during sulfonation. This was also confirmed by the presence of the XRD diffraction peak (2θ = 35°–50°) in HTCDRB-SO_3H. In addition, the appearance of sulfonic groups, suggested by the bands at 1072 cm^{-1} (-SO_3^{2-} stretching modes in $-SO_3H$ group) and 1265 cm^{-1} (symmetric OS=O stretching vibrations of sulfonic groups), indicated that sulfonated HTC-based catalysts were successfully prepared (Nakhate and Yadav, 2016). This was also suggested by the increase in the contents of sulphur, sulfonic group as well as the total acidity, both in HTCDRB-SO_3H and HTCG-SO_3H catalysts, as can be seen in Table 2. In addition to the XRD and the FTIR results, BET surface areas of the HTCs and the corresponding HTC-SO_3H catalysts from DRB and glucose were also measured. All samples were found to possess rather small surface areas ($< 10\ m^2\ g^{-1}$).

TGA patterns of HTC and the corresponding HTC-SO_3H are shown in

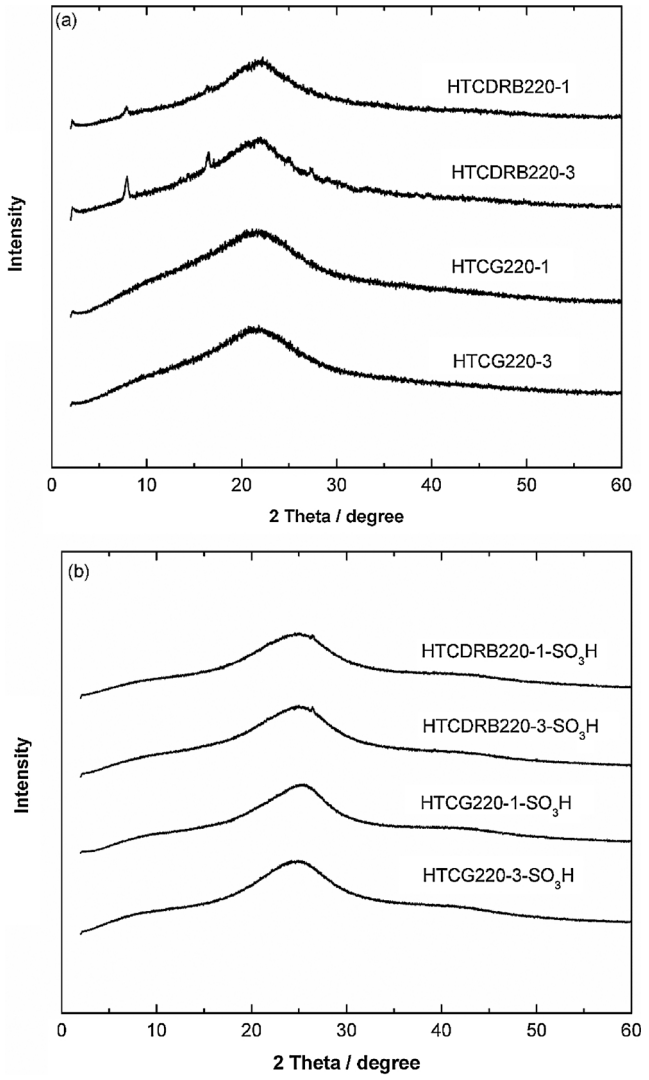

Fig. 3. XRD patterns of (a) HTCs and (b) HTCs-SO_3H catalysts prepared from DRB and glucose. Hydrothermal carbonization temperature was 220 °C and times were 1 and 3 h.

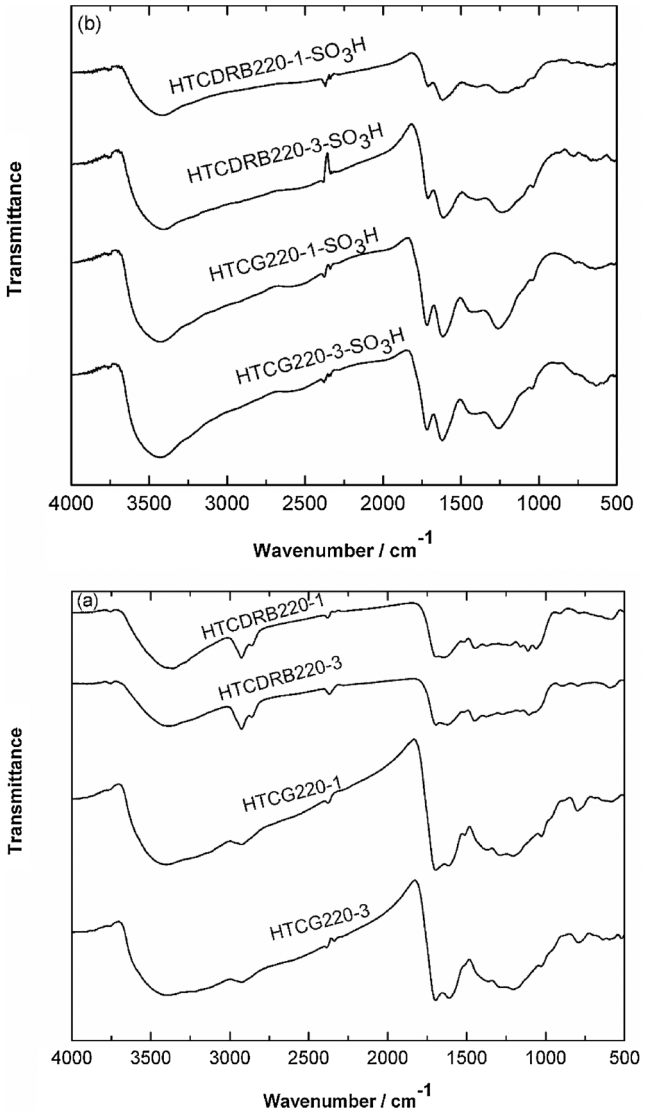

Fig. 4. FTIR spectra of (a) HTCs and (b) HTCs-SO_3H catalysts prepared from DRB and glucose by hydrothermal carbonization temperature of 220 °C for 1 and 3 h.

Fig. 5(a) indicates that the HTCDRB has lower thermal stability than the HTCG, while on the other hand, the thermal stability of the HTCDRB-SO_3H was slightly higher than HTCG-SO_3H (Fig. 5(b)). The weight loss of HTCG and HTCG-SO_3H followed the same trend, while the weight loss characteristics of HTCDRB and HTCDRB-SO_3H appeared to be different. Three major weight loss regions were observed for HTCDRB. The first weight loss of about 2% occurred at the temperatures below 140 °C, which was attributed to the loss of water and free moisture adsorbed on the carbon surface. The second weight loss took place in the temperature range between 140 and 350 °C, attributing to the loss of HTCDRB structural components such as hemicellulose, cellulose and lignin. Corresponding to the decomposition temperature of hemicelluloses at 180 °C, and that of cellulose and lignin at 220 °C (Reza et al., 2014), the initial weight loss was related to hemicellulose loss that occurred sluggishly, followed by more rapid weight losses of cellulose and lignin, as well as the remaining hemicellulose toward the end of this interval. Lastly, the rapid weight loss at temperatures above 350 °C was attributed to the loss of the remaining char, caused by the decomposition of the remaining cellulose and lignin structure (Islam et al., 2015). For HTCDRB-SO_3H, three distinctive weight loss regions were found. The first rather rapid water loss occurred below 100 °C. The second weight loss occurred as the remaining moisture sluggishly evaporated at the temperature between 100 and 200 °C. The last weight loss occurred at above 200 °C, was observed upon the thermal decomposition of SO_3H (Kang et al., 2013; Malins et al., 2015). Based on the TGA results, HTCDRB-SO_3H and HTCG-SO_3H appeared to be stable at temperatures below 250 °C, and were suggested to be suitable for reactions under this temperature.

3.3. Catalyst leaching under hydrothermal reaction condition

Since the catalyst was prepared by sulfonation of hydrothermally carbonized DRB, when it is applied to chemical reactions such as biomass conversion, it should be ensured that the prepared HTC-SO_3H catalyst itself does not undergo the conversion that would interfere with the reaction of interest. For this reason, under a specified biomass hydrolysis condition (200 °C and 5 min under microwave irradiation), the leaching of biomass conversion products from the catalyst into water was evaluated. The photographs of the liquid fractions obtained after the leaching experiments are shown in Fig. S1. From this figure, the liquid fractions for the glucose derived HTC-SO_3H catalyst appeared to have red brown color, implying that large amounts of biomass conversion products (i.e. HMF, furfural, levulinic acid and formic acid) were leached out from the HTCG-SO_3H catalysts. It is noted from this results that even though the catalysts were washed repeatedly with boiling distilled water to remove chemical residues from the catalyst

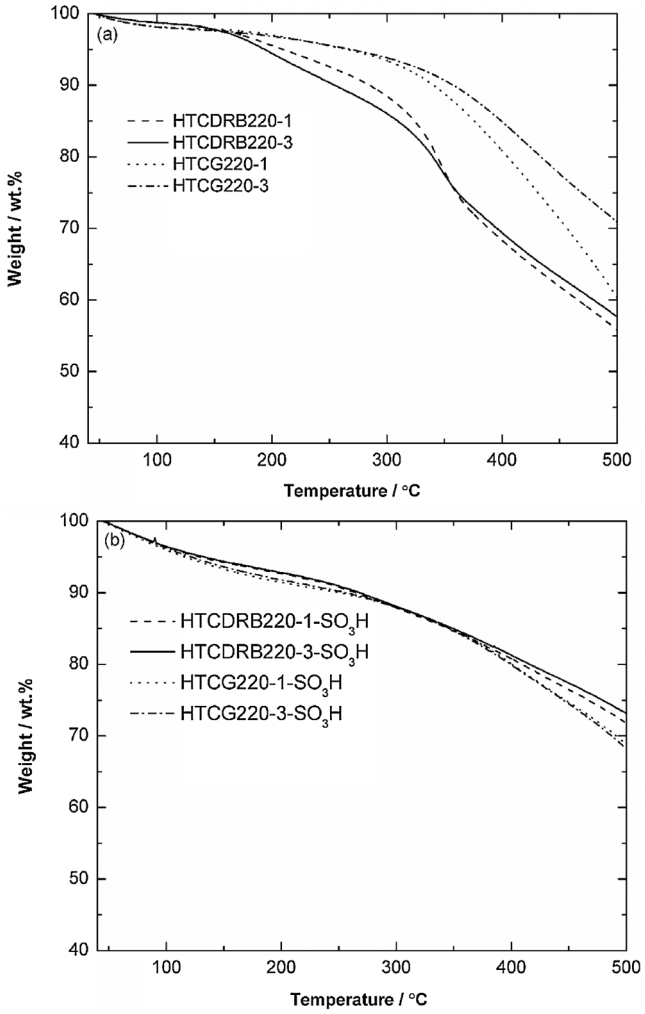

Fig. 5. TGA patterns of (a) HTCs and (b) HTCs-SO_3H catalysts prepared from DRB and glucose. Hydrothermal carbonization temperature was 220 °C and times were 1 and 3 h.

Table 2
Contents of sulphur, sulfonic group and total acidity of HTCDRB and HTCG (carbonization temperature of 220 °C for 1 and 3 h) and of sulfonated HTCDRB and HTCG based catalysts.

Sample name	Sulphur (wt. %)	Sulfonic group (μmol g^{-1})	Total acidity (μmol g^{-1})
HTCDRB220-1	0.5	0.0	809
HTCDRB220-3	0.5	0.0	745
HTCG220-1	0.0	0.0	634
HTCG220-3	0.0	0.0	647
HTCDRB220-1-SO_3H	1.3	35.4	1064
HTCDRB220-3-SO_3H	1.4	33.9	1017
HTCG220-1-SO_3H	0.8	39.8	1083
HTCG220-3-SO_3H	1.0	45.8	1117

during their preparation, this washing process could not guarantee that the catalyst would not further undergo chemical reactions. The liquid fractions obtained by DRB derived HTC-SO_3H catalysts, on the other hand, were found to have light yellow color, thus implying that small amounts of biomass conversion products were leached from the catalysts. These liquid fractions were also analysed via HPLC and the results are shown in Fig. 6. As shown in Fig. 6, the leaching of biomass conversion products from both the HTCDRB-SO_3H and HTCG-SO_3H catalysts decreased (catalyst stability increased) with increasing carbonization time from 1 to 3 h. It can be implied from Fig. 6 that the stability of HTCDRB-SO_3H was higher than that of the HTCG-SO_3H catalyst

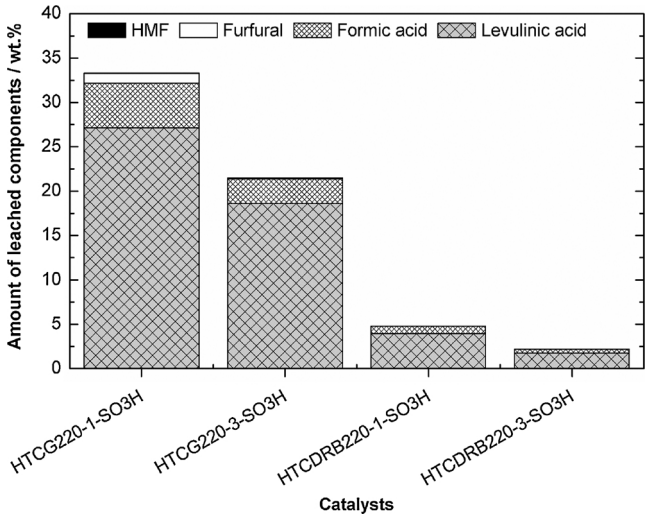

Fig. 6. Amounts of leached component (i.e. HMF, furfural, levulinic acid and formic acid) in liquid fraction of HTCs-SO_3H hydrolysis under microwave at temperature of 200 °C for 5 min.

prepared at the same carbonization condition, since the amounts of leached components (i.e. HMF, furfural, levulinic acid and formic acid) from the HTCDRB-SO_3H catalysts were considerably lower. The higher stability of HTCDRB-SO_3H could be attributed to the difference in the HTC formation mechanisms as seen earlier and as suggested in previous literatures (Kang et al., 2012; Lei et al., 2016; Titirici et al., 2012). Starting with glucose in an aqueous solution, HTCG was formed largely via glucose dehydration to HMF, which, upon condensation, aromatized HTC structures were subsequently formed. While starting with DRB on the other hand, the HTCDRB was formed partly via biomass hydrolysis, followed by glucose dehydration, and condensation and aromatization, and partly by the direct condensation and aromatization of the biomass raw material. With the direct route that was also undertaken, it would be expected therefore that, at the same carbonization condition, a more highly stable and aromatized HTC could be obtained from DRB. It is noted that at the hydrothermal carbonization temperature of 220 °C for 3 h (HTCDRB220-3-*S*O_3H), no HMF and furfural, and only relatively small amounts of levulinic acid (1.75 wt.%) and formic acid (0.42 wt.%) were leached from that catalyst. This suggested that the HTCDRB220-3-*S*O_3H catalyst was relatively stable and could suitably be used to prepare a HTC-based catalyst for biomass conversion.

3.4. Catalyst activity on cellulose hydrolysis

HTCDRB220-3-SO_3H was tested toward cellulose hydrolysis in subcritical water at 180 °C for 5 min with 5 wt.% catalyst loading. The glucose, HMF, and furfural yields were measured and the results were compared to those from the reaction obtained under non-catalytic condition, and with commercial sulfonated solid catalyst-Amberlyst 16 WET at the same operating conditions. The results shown in Fig. 7 revealed that both HTCDRB220-3-SO_3H and Amberlyst 16 WET have catalytic activities over cellulose hydrolysis, with HTCDRB220-3-SO_3H giving 19% higher glucose and 46% higher HMF yields, respectively. The furfural yields were not significantly different possibly due to very small amounts of furfural in both reactions. It should be noted also that the glucose yield obtained from cellulose hydrolysis catalysed by HTCDRB220-3-SO_3H in this study (49.6 wt.%) was comparable to that of the reaction catalysed by sulfonated activated carbon (AC-SO_3H) (48.9 wt.%) at 150 °C for 24 h (Onda et al., 2009), and higher than those (15–30 wt.%) of the reactions catalysed by other sulfonated catalysts such as Amberlyst 15, Si-based catalyst (Si66C33-823-SO_3H), and sulfonated zirconia, also carried out at 150 °C for 24 h (Huang and Fu,

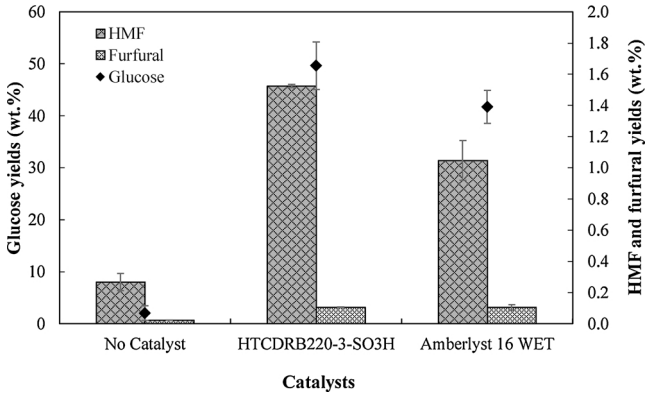

Fig. 7. Amounts of glucose, HMF and furfural in liquid products of cellulose hydrolysis in subcritical water at 180 °C and 5 min and 5 wt.% catalyst loading, catalysed by HTCDRB220-3-*S*O_3H and Amberlyst 16 WET.

2013; Onda et al., 2009).

4. Conclusions

HTCDRB was successfully prepared by hydrothermal carbonization of DRB, and was further functionalized with sulfuric acid to prepare a HTCDRB-SO_3H catalyst. The yield, the morphological structures, and the chemical characteristics of the HTCDRB and HTCDRB-SO_3H catalyst, as well as the stability of the catalyst were compared with those of the glucose derived HTCG and HTCG-SO_3H catalyst. While the chemical characteristics of the HTC and HTC- SO_3H catalysts prepared from DRB and glucose were similar, the HTCDRB and HTCG have completely different morphological structures, with HTCDRB having highly complex structure and HTCG having spherical form. The TGA results suggested that, even though the thermal stability of HTCDRB was lower than that of HTCG, the thermal stability of HTCDRB-SO_3H was apparently higher than that of HTCG-SO_3H. Based on the results of the leaching tests, hydrothermal carbonization at 220 °C and 3 h was found to be most suitable for the preparation of HTCDRB-SO_3H, while the preparation of HTCG-SO_3H would require higher carbonization conditions. Moreover, the HTCDRB220-6-SO_3H showed higher catalytic activities on cellulose hydrolysis than the commercial sulfonated solid Amberlyst 16 WET catalyst. Further tests of the catalyst leaching in solvothermal reaction systems for biomass conversion are suggested.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.indcrop.2018.03.002.

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Short communication

Preparation of hydrothermal carbon as catalyst support for conversion of biomass to 5-hydroxymethylfurfural

Piyaporn Wataniyakul[a], Panatpong Boonnoun[b], Armando T. Quitain[c], Mitsuru Sasaki[c], Tetsuya Kida[c], Navadol Laosiripojana[d], Artiwan Shotipruk[a,*]

[a] Chemical Engineering Research Unit for Value Adding of Bioresources, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Phayathai Road, Patumwan, Bangkok 10330, Thailand
[b] Department of Industrial Engineering, Faculty of Engineering, Naresuan University, Phitsanulok 65000, Thailand
[c] Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860-8555, Japan
[d] The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Prachauthit Road, Bangmod, Bangkok 10140, Thailand

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ABSTRACT

Suitable hydrothermal carbonization conditions including temperature (180–250 °C) and time (6–24 h) were determined for the preparation of glucose derived carbon material, used as a catalyst support for sugar and cellulose conversions. While hydrothermal carbons (HTCs) prepared at various conditions exhibited similar chemical and structural characteristics, examination of liquid fractions from hydrothermal carbonization provided additional evidence on the stability of the HTCs. The suitable hydrothermal carbonization condition was found to be 220 °C and 6 h, providing a stable carbon support that after sulfonation, yielded carbon-based acid catalyst (HTC220-6-SO_3H) that exhibit relatively high catalytic activities for cellulose hydrolysis and fructose dehydration reaction, giving glucose and HMF yields of 43.63 ± 1.62 wt.% and 20.29 ± 1.09 wt.%, respectively.

1. Introduction

5-Hydroxymethylfurfural (HMF) has recently been identified as one of the most important biomass-derived platform chemicals for the production of fuels, furan-based polymers, as well as fine chemicals and pharmaceuticals [1]. HMF production from biomass involves hydrolysis of biomass cellulose and hemi-cellulose to monomer sugars (i.e. glucose and xylose), and further dehydration of these monomer sugars to furan compounds, such as HMF and furfural. The reactions generally take place in hot compressed water at self-generated pressure, typically in presence of high acidity catalyst. Early research in biomass conversion to HMF focused on the use of homogeneous mineral acids, such as H_2SO_4, as catalysts [2,3]. However, such homogeneous catalysts have a number of disadvantages including equipment corrosion, environmental pollution and difficult recovery and reuse [4]. Alternatively, various types of heterogeneous acid catalysts: transition-metal oxides [5,6], heteropoly acids [7,8] and carbon-based acid catalysts [9], have recently been investigated for their reactivity toward HMF production. Among these heterogeneous catalysts, carbon-based acid catalysts are gaining considerable interests, due to simple synthesis procedure and low cost carbon materials (i.e. sugars, carbohydrates, or lignocellulosic biomass). Carbon-based acid catalysts can be synthesized by initially preparing a catalyst support by pyrolysis/carbonization of a starting carbon material at high temperature (above 400 °C) [10,11]. Then, the surface chemical modification of the achieved carbon-based catalyst is typically performed by acid functionalization [10,12]. Generally, carbonization takes place at relatively high temperatures. When biomass with high moisture content is used as a starting carbon source, additional heat is needed to ensure water is completely removed, making the process even more severely energy intensive. Recently, a new approach for preparation of carbon material via *hydrothermal carbonization* has been devised. In this process, carbonization takes place in water at milder temperatures (150–250 °C). Importantly, this process can convert wet raw material into carbonaceous solid without the need for prior drying [13]. The mechanism of HTC formation from biomass consists of 4 steps; (i) cellulose is hydrolyzed to glucose, (ii) glucose is then dehydrated to HMF, (iii) HMF is polymerized and aromatized to form aromatic units, and (iv) the aromatic units are condensed to form *hydrothermal carbon* (HTC) [14]. This rather new carbon material has potentially been applied in various applications including adsorbent [15], fuel source [16], energy storage [17], and catalysis [18]. For each application, the proper production of HTC requires different suitable

* Corresponding author.
E-mail address: Artiwan.Sh@chula.ac.th (A. Shotipruk).

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hydrothermal carbonization conditions. For catalysis application, important HTC preparation conditions include hydrothermal temperature and time, from which the temperature could be ranged from 180 to 250 °C and the time could be between one to several hours [19]. After hydrothermal, the HTC could be further functionalized with various acids for applications in high acidity catalyzed reactions e.g. esterification [20,21], transesterification [22], hydrolysis [18], and dehydration reactions [23].

The aim of this study is to determine proper hydrothermal conditions including hydrothermal temperature and time, for the preparation of glucose-derived HTC and use as catalyst support for biomass-derived compound conversion. Provided with the fact that the first two steps of HTC formation follow the exact same paths of HMF production, it is of utmost importance therefore, to ensure that the catalyst derived from a HTC support is stable enough that, by itself, does not decompose and form HMF. To the best of our knowledge, this study is the first that thoroughly evaluates the stability of the HTC produced specifically for the purpose of biomass conversion. By checking not only the characteristics of the solid HTC, but also the compositional analyses of the aqueous reaction fraction, the suitable carbonization conditions were proposed. Moreover, the catalytic activity of the sulfonated carbon-based acid catalyst (HTC-SO_3H) prepared from the HTC produced at suitable condition was examined for biomass conversion including cellulose hydrolysis and fructose dehydration. Lastly, the stability of the catalyst was also tested based on the recyclability of the catalyst in fructose dehydration.

2. Materials and methods

2.1. Materials and chemicals

Glucose, fructose, sulfuric acid, ethanol and acetone were purchased from Wako Pure Chemical Company (Osaka, Japan). All analysis chemicals including 3,5-dinitrosalicylic acid (DNS), potassium sodium (+) – tartrate tetrahydrate, sodium hydroxide, perchoric acid, acetic acid and methanol were also purchased from Wako Pure Chemical Company (Osaka, Japan). Cellulose powdered was purchased from HiMedia Laboratories Pvt. Ltd. (Mumbai, India).

2.2. Preparation of sulfonated HTC-based catalyst

The sulfonated HTC-based catalyst was prepared from glucose following a two-step process, hydrothermal carbonization of glucose to produce glucose based HTC as a catalyst support, followed by functionalization of the resulting HTC with sulfuric acid.

Firstly, HTC was prepared by hydrothermally carbonizing glucose in a 520 ml SUS-316 stainless steel closed batch reactor (OM LABTECH Co., Japan). 30 g of glucose and 300 ml of de-ionized water were charged in the reactor. The mixture was stirred and heated with an electric heater to a desired temperature (180–250 °C), which took approximately 15–35 min heating time. At the desired temperature, carbonization reaction was allowed to proceed for a holding period of 6–24 h, after which the reactor was cooled to room temperature by an electric fan. The solid HTC and liquid fraction of the reaction were then removed from reactor and were separated by means of vacuum filtration. The liquid fraction was analyzed to determine the amount of glucose and HMF, as well as total reducing sugar (TRS). The solid HTC was washed with three solvents in the following sequence: de-ionized water, ethanol, and followed by acetone, in order to remove polar chemicals such as levulinic acid and formic acid produced during the reaction. For each washing step, HTC was mixed with 500 ml of solvent and the mixture was sonicated for 1 h. The HTC was then separated from the solvent by vacuum filtration, and was dried at 60 °C for 24 h. The resulting HTC was stored in a desiccator for subsequent use. Based on the preparation conditions, the HTC was labeled as HTCX-Y, where X (X = 180, 220, 250 °C) represents the hydrothermal carbonization temperature and Y (Y = 6, 12, 18, 24 h) represents the hydrothermal carbonization time. The HTC yield was determined as the percentage of weight ratio (dry basis) of the produced HTC and the raw material (glucose).

Then, HTC-SO_3H was prepared by sulfonation following the method described by Okamura et al. (2006) [24]. Briefly, 5 g of HTC was heated in 50 ml of concentrated H_2SO_4 (> 96%) at 150 °C for 15 h in a 3-neck round bottom flask. The resulting solid acid catalyst was then washed with 1000 ml of distilled water, and was further washed with boiling distilled water until no pH change in the wash water was observed. The resulting solid catalyst was subsequently washed with 500 ml of ethanol and then with 300 ml of acetone, and was dried overnight at 60 °C.

2.3. Catalyst characterizations

The elemental analysis (C, H, and N) of HTC and HTC-SO_3H samples was carried out using elemental analyzer (J-Science Lab Micro Corder JM10), and the sulfur content was carried out using elemental analyzer (J-Science Lab Micro Corder JMSU10). The oxygen content was calculated by subtraction of C, H, N, and S from 100%. The crystallinity analysis of the samples was examined using automatic X-ray diffractometer (XRD; RINT 2100, Rigaku) performed using Miniflex Guidance software. Each sample was scanned in the range of 3–90°. The surface morphologies of samples were acquired with Field Emission Scanning Electron Microscopy (FESEM, JSM-7610F) operated at 2.0 kV. Functional groups of samples were determined by Fourier transform infrared (FTIR) spectra using Jasco FT-IR-4100 spectrometer (JASCO International Co., Japan). Prior to measurement, the sample was grounded into fine particles and mixed with KBr to prepare disks. Each sample was investigated in the wavenumber range of 4000–500 cm^{-1} with resolution of 4 cm^{-1}. The thermogravimetric analysis was conducted to determine the thermal stabilities of the samples using a thermogravimetric analyzer (TGA; TG/DTA6200, SII EXSTAR 6000, Hitachi High-Technologies Corporation, Japan). Non-isothermal combustion of all samples was conducted in the furnace of the TGA system under a nitrogen gas atmosphere at a flow rate of 10 ml/min and a heating rate of 10 °C/min from the starting temperature of 45 °C to 500 °C. The sample weight loss was continuously recorded under the experimental conditions. The specific area, pore volume and pore size diameter of all HTC and HTC-SO_3H were determined by N_2 physisorption technique using the Brunauer-Emmet-Teller (BET) method with a Belsorp-mini (BEL Japan, Tokyo, Japan); the samples were pretreated to remove moisture at 150 °C for 3 h prior to measurement. The total acidity of the samples was analyzed by temperature-programmed desorption (TPD) with ammonia [25].

Apart from solid characterization, the TRS obtained in the liquid fraction of hydrothermal carbonization of glucose was analyzed by a dinitrosalicylic (DNS) colorimetric method, using D-glucose as a standard [26]. Into each 1 ml of the sample, 2 ml of de-ionized water and 3 ml of DNS reagent were mixed. The mixture was then heated in boiling water for 5 min until the red-brown color was developed. The mixture was then cooled to room temperature in a water bath. The absorbance was measured with a spectrophotometer (JASCO V-660 UV-VIS Spectrophotometer, JASCO International Co., Japan) at 540 nm. The amount of TRS was determined using standard calibration curve and % TRS was calculated based on the weight percent of the starting glucose.

The quantification of glucose and HMF components obtained in liquid fraction were conducted using a high performance liquid chromatography (HPLC, JASCO International Co., Ltd., Japan) which consist of a Jasco RI-2031 plus detector, Jasco UV-970 detector, Jasco PU980 pump system, sugai U-620 column heater and a Jasco AS-2055 plus automated sampler injector equipped with a Shodex SUGAR SH1011 (8.0mmID × 300 mm) column. The column temperature was set at 60 °C and the injection volume was set at 10 µl, and perchoric

acid ($HClO_4$) was used as an eluent at a flow rate of 0.5 ml/min. Glucose and HMF were analyzed with detected by the refractive index (RI) detector, and the UV detector at 220 nm, respectively. The concentrations of glucose (retention time = 16.2 min) and HMF (retention time = 39 min) were calculated using external calibration curves attained from standard solutions of known concentrations. The analyses of HMF and glucose allowed the determination of HMF content, defined as weight percentage of HMF to the starting glucose, and the glucose conversion, percentage of the mass difference between the starting glucose and the glucose remained in the liquid product, over the mass of the starting glucose.

2.4. Catalytic activity test

Both synthesized HTC and HTC-SO_3H were tested toward the cellulose hydrolysis and fructose dehydration. It is noted that the commercial grade sulfonated solid catalyst-amberlyst 16 wet (Fluka Analytical, Sigma-Aldrich Chemie GmbH), and graphene oxide (GO) prepared by modified Hummer's method [27] were also tested for comparison. The reaction was carried out in an 8.8 ml SUS-316 stainless steel closed batch reactor (Suan Luang Engineering Ltd., Part.), from which 0.1 g of raw material (cellulose or fructose), 5 ml of deionized water, and 0.005 g of catalyst (5 wt.% of raw material) were charged. The reactor was shaken and heated to the desired reaction temperature (180 °C) by an electric heater, with a temperature controller connected to it. After the reaction, the reactor was quenched in a water bath at room temperature to stop the reaction. With additional amount of 5 ml of de-ionized water, the solid and liquid reaction products were completely removed from the reactor, and were separated from each other by whatman filter paper no 1. The amounts of glucose, fructose, HMF and furfural in the liquid product were determined by HPLC.

The quantification and identification of glucose and fructose in the liquid products were conducted using an HPLC equipped with an evaporative light scattering detector (ELSD) detector with a Rezex RPM Monosaccharide Pb + 2 (7.8 mmID * 300) column at 60 °C. Injection volume was set at 5 μl and water was used as the eluent at a flow rate of 0.6 ml/min. The retention times of glucose and fructose were 13.3 and 19.0 min, respectively. The analysis for the amount of HMF and furfural were carried out using a Varian C18 (4.6 mmID * 250) column at 25 °C, with 90% (1% aq. Acetic acid):10% methanol used as the eluent. The eluent flow rate was 1 ml/min, and the injection volume was set at 10 μl. The concentration of HMF and furfural were analyzed based on UV absorbance at 285 nm. The retention times of HMF and furfural were 6.6 min and 9.0 min, respectively. The yields of the reaction products: glucose, HMF and furfural were calculated as mass percentages of the products to the mass of the starting material (cellulose or fructose). The conversion of fructose was defined as the percentage of the mass difference of the starting fructose and the fructose remained in the liquid product, over the mass of the starting fructose.

It is noted that the recyclability of HTC-SO_3H was also performed. After the first cycle of fructose dehydration test, the catalyst was separated from the reaction medium by means of filtration and washed with the deionized water until no pH change in the wash water was observed. The recovered catalyst was then washed with 30 ml of ethanol and 10 ml of acetone, and dried overnight, and reused for five cycles.

3. Results and discussion

3.1. Synthesis of HTC by hydrothermal carbonization of glucose

The HTC yields obtained by hydrothermal carbonization of glucose at various conditions are shown in Table 1. As the temperature increased from 180 °C to 220 °C, HTC yield was found to increase with increasing temperature, suggesting that the degree of glucose carbonization increased as the temperature increased. As the temperature increased from 220 °C to 250 °C, the increase in the HTC yield shows a diminishing return, after reaching approximately 30–33 wt.%. Similar trends were also reported by Falco et al. that increasing hydrothermal carbonization temperature from 160 °C to 200 °C, the glucose derived HTC yield increased [28]. Nevertheless, the glucose derived HTC yield stayed relatively constant at the hydrothermal carbonization temperature higher than 200 °C. For the effect of carbonization time, it was found that at low carbonization temperature of 180 °C, HTC yield increased from 6.51 wt.% to 28.53 wt.% as the carbonization time increased from 6 h to 24 h. At higher carbonization temperatures of 220 °C and 250 °C, the yield of HTC derived from hydrothermally carbonized glucose was insignificantly increased with increasing carbonization times. The morphological structures of HTCs produced at various carbonization conditions as shown in Fig. 1 suggested that the glucose derived HTC particles are of spherical shape, with smooth surfaces, and having approximate size ≥ 0.25 μm. It was also revealed from these SEM images that the increase in carbonization times not only affected the growth of individual particles, but also the particle agglomeration. From BET measurement, the surface area, pore volume and pore size diameter of the HTC samples were approximately 1.66–4.04 $m^2 g^{-1}$, 0.0023–0.0096 $cm^3 g^{-1}$, and 5.70–11.80 nm, respectively (Table S1).

The elemental analyses of glucose before and after hydrothermal carbonization are summarized in Table 1. The hydrothermal carbonization of glucose led to an increase in carbon content from 39.69 wt.% to 63.62–69.09 wt.%. In contrast, the amount of oxygen and hydrogen decreased in all HTC samples, suggesting dehydration as well as aromatization and condensation took place during hydrothermal carbonization. Moreover, the decrease of H/C ratio from 0.178 in glucose to 0.056–0.064 in HTC and of O/C ratio from 1.339 in glucose to 0.385–0.507 in HTC also confirmed that after hydrothermal carbonization, HTC had high level of aromaticity [29,30]. It was also revealed from this study that the carbonization temperature shows greater impact on the product characteristics than the carbonization time. The percentage of carbon was slightly increased when the temperature of hydrothermal carbonization increased from 180 °C to 250 °C. As the temperature increased, the O/C ratio decreased but H/C ratio was nearly constant. This indicated that dehydration (water was removed from glucose) almost reached completion, while decarboxylation (production of carboxyl including carboxylic acid) became more prominent [31]. The elemental data therefore suggested the mechanism of hydrothermal carbonization to involve glucose dehydration to HMF, the aromatization of HMF to aromatic unit, and finally the condensation of aromatic unit to aromatic carbon. Aromatic carbons or HTC samples, confirmed by crystallinity analyses, were amorphous carbon structures, with broad C diffraction peak (2θ = 15°–30°) (Fig. S1). Similar results have been reported by Okamura et al. (2006) [24].

As shown in Fig. S2, the FTIR spectra of all HTC samples are similar to those of HTC from glucose in saline solution reported previously [32]. The bands at approximate range of 875–750 cm^{-1} were assigned to aromatic C—H out-of-plane bending vibrations, whereas the bands at 1600 cm^{-1} corresponded to stretching vibrations of aromatic C=C. The existence of these bands suggested that aromatization took place during carbonization reaction. Moreover, the HTC samples were found to contain several bonds associated with acid functional groups. The bands at approximately 1710 cm^{-1} and those lied in the range between 3700 and 3000 cm^{-1} corresponded to stretching vibrations of aromatic C=O (carbonyl, ester, or carboxyl) and hydrogen bonded O—H (hydroxyl or carboxyl group), respectively, suggesting carboxylic acid group occurred as a result of hydrothermal carbonization process [30].

Similar trends on the TGA results were observed for all of HTC samples as shown in Fig. S3. The HTC samples were found to be thermally stable at temperature below 300 °C, with insignificant weight loss (< 6%) observed. The rapid weight loss at the temperature above 350 °C on the other hand, was possibly due to the decomposition of acids such as hydroxyl and carboxyl groups from the carbon structure. The recommended reaction temperatures would therefore be below

Table 1
HTC yields and elemental compositions of carbonaceous materials before and after hydrothermal carbonization.

Sample name	Conditions		Elemental Compositions					HTC Yield (wt.%)
	T (°C)	t (h)	C (wt.%)	H (wt.%)	O (wt.%)	Atomic ratios		
						H/C	O/C	
Glucose	–	–	39.680	7.065	53.145	0.178	1.339	–
HTC180-6	180	6	63.620	3.970	32.285	0.062	0.507	6.913
HTC180-12	180	12	63.765	3.940	32.235	0.062	0.506	17.957
HTC180-18	180	18	64.285	3.980	31.600	0.062	0.492	24.318
HTC180-24	180	24	64.685	3.980	31.205	0.062	0.482	28.527
HTC220-6	220	6	65.815	4.030	30.015	0.061	0.456	29.583
HTC220-12	220	12	66.790	4.130	28.950	0.062	0.433	31.649
HTC220-18	220	18	66.485	4.180	29.205	0.063	0.439	31.983
HTC220-24	220	24	66.900	4.250	28.730	0.064	0.429	32.630
HTC250-6	250	6	68.105	3.990	27.740	0.059	0.407	32.531
HTC250-12	250	12	69.085	4.135	26.630	0.060	0.385	31.869
HTC250-18	250	18	68.745	3.975	27.150	0.058	0.395	33.118
HTC250-24	250	24	69.060	3.850	26.975	0.056	0.391	33.383

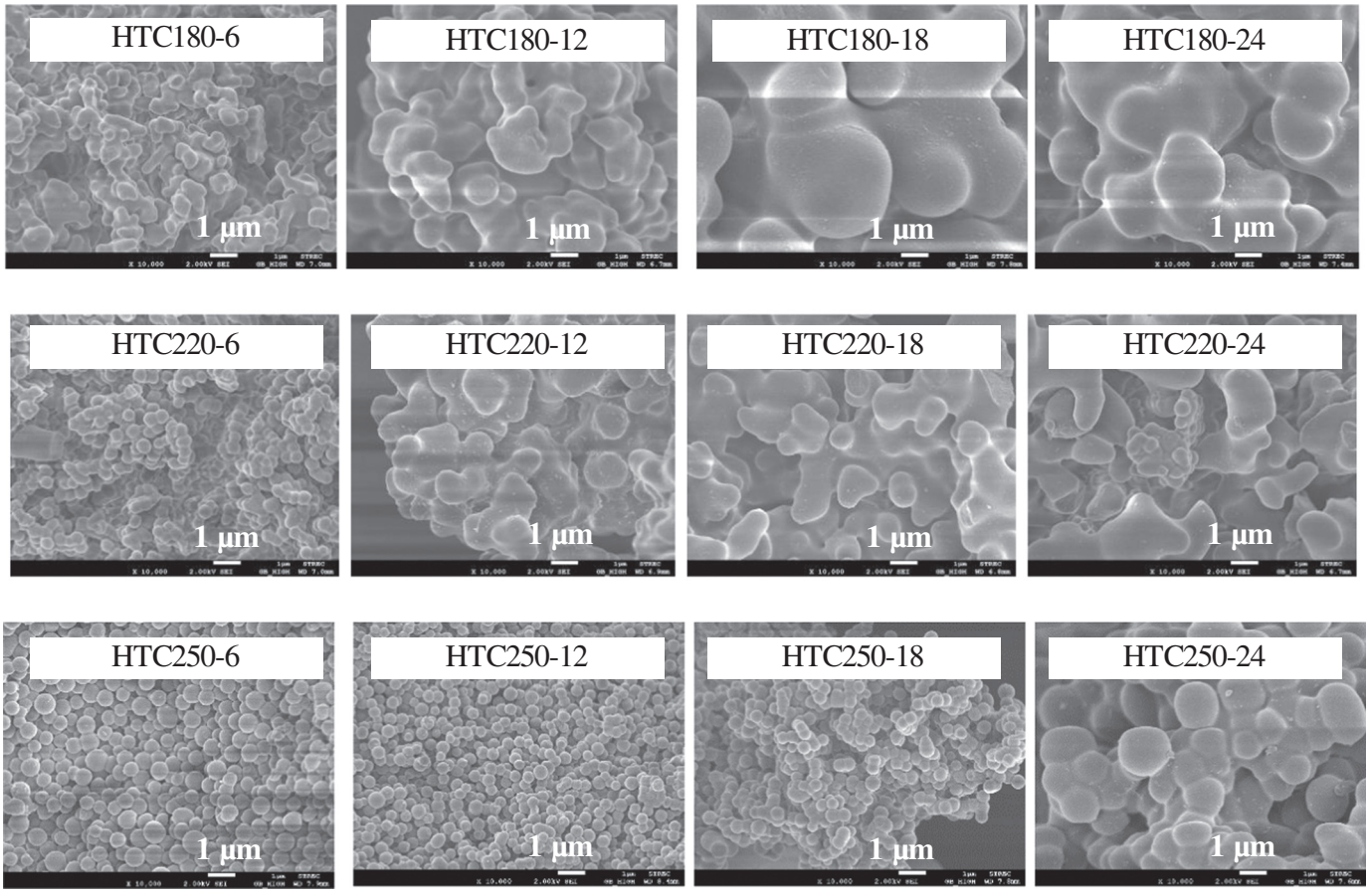

Fig. 1. SEM images of HTCs prepared by hydrothermal carbonization at various temperatures and times.

300 °C.

In this study, the approach to confirm the stability of the HTC-based acid catalyst is to ensure that complete carbonization was achieved during the preparation of HTC. Specifically, the liquid fraction after carbonization must contain the minimum amount of sugar (glucose in this case) and furan compounds (i.e. HMF). The amounts of TRS, glucose and HMF in liquid fraction from reactions under various hydrothermal carbonization conditions were therefore analyzed. The results shown in Fig. 2 suggested that the highest TRS was found in the liquid fractions obtained at temperature of 180 °C after 6 h, and tended to decrease as the carbonization time increased from 6 h to 24 h. This implied that at 180 °C, the reducing sugar still continued to decompose to other chemicals (i.e. HMF) as the reaction time increased. While at higher hydrothermal carbonization temperature at 220 °C and 250 °C, the TRS in the liquid fractions stayed relatively constant for all hydrothermal carbonization times. The %TRS results corresponded to the glucose conversion, in which higher glucose conversion was found at longer carbonization time at 180 °C, and the complete conversion of glucose was observed at high temperatures: 220 °C and 250 °C.

It should be noted that the results of liquid fraction analysis are in good agreement with those of the HTC yield. Specifically, at low carbonization temperature of 180 °C, the change in glucose conversion and

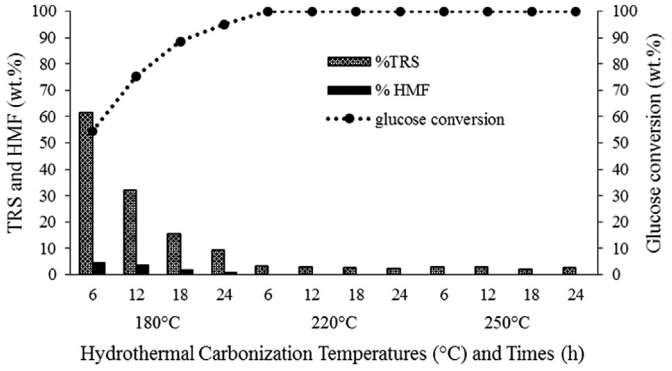

Fig. 2. Glucose conversion, %TRS and HMF of hydrothermal carbonization liquid fractions at various temperatures and times.

HMF content with carbonization time was observed, which correspond to the increase in the HTC yield with increasing time. On the other hand, at higher temperatures of 220 °C and 250 °C, 100% glucose conversion had been reached after 6 h, and remained unchanged with carbonization time, which corresponded to results of relatively no HMF content in liquid fraction and those of relatively high and unchanged HTC yields with time. It can be drawn from the above results that the proper hydrothermal carbonization conditions required for the preparation of HTC for biomass conversion should be above 220 °C and 6 h.

3.2. Sulfonation of HTC

HTC prepared at 220 °C for 6 h (HTC220-6) was selected as a catalyst support, and was further sulfonated to obtain a HTC220-6-SO_3H catalyst. Its catalytic activity toward the production of HMF from biomass was subsequently determined.

As shown in the supplementary data, HTC220-6-SO_3H and HTC220-6 were found to have similar XRD patterns (Fig. S4a). The broad C diffraction peak (2θ = 15–30°) can be attributed to the amorphous carbon structures. The XRD patterns of carbons before and after sulfonation showed no noticeable difference, suggesting that sulfonation process had no effect on carbon structure. On the other hand, according to the SEM images of HTC220-6-SO_3H and HTC220-6 in Fig. S4b, HTC220-6-SO_3H clearly possesses rougher surfaces, which possibly due to the surface coverage of the HTC220–6 with sulfuric acid. The surface area of the HTC220-6-SO_3H was also found to be higher than that of the HTC220-6 (Table 2). In addition, the adsorption-desorption isotherm, the supplementary data (Fig. S5), of HTC220-6-SO_3H indicated that HTC220-6-SO_3H is of type IV isotherms with evident hysteresis loops in the relative pressure range of about 0.79–0.97. In addition, the decrease in the pore volume and the pore size from 0.006 $cm^3\ g^{-1}$ and 11.311 nm in HTC220-6 to 0.005 $cm^3\ g^{-1}$ and 4.274 nm in HTC220-6-SO_3H, respectively, implied the presence of sulfuric acid within the pores. Furthermore, as a result of sulfonation, the acidity and the sulfur content of HTC220-6-SO_3H increased to 7.944 (from 6.620) mmol g^{-1} and to 0.709 (from 0) mmol g^{-1}, respectively (Table 2).

The FTIR spectrums of HTC220-6 and HTC220-6-SO_3H (Fig. S4c) clearly indicated the presence of SO_3H group in the latter, confirmed by the stretching vibration bands of O═S═O and $-SO_3^{2-}$ at 1167 and 1027 cm^{-1}, respectively. Based on FTIR result, the hydrothermal glucose based acid catalyst prepared in this study (HTC220-6-SO_3H) is similar to the carbon-based catalyst prepared from microalgae residue [33].

Moreover, the TGA result (Fig. S4d) demonstrated that the thermal stability of HTC220-6-SO_3H was lower than that of HTC220-6, possibly due to the decomposition of SO_3H group. In addition, thermal stability of HTC220-6-SO_3H was found to be similar to that of the hydrothermal carbon-based catalyst derived from D-xylose (D-SO_3H) reported by Kang et al. [34], except for the slight water loss observed below 100 °C, observed in D-SO_3H but not in HTC220-6-SO_3H. This difference was possibly explained by the fact that the HTC220-6-SO_3H was more completely dried after the washing step with water, ethanol and acetone. Nevertheless, the decomposition characteristics of both catalysts were identical, from which rapid decomposition started to occur at 250 °C. Therefore, temperatures below 250 °C were suggested to be suitable for reaction condition.

Table 2
Surface area, pore volume, pore size, total acidity, and sulfur content of HTC220-6 and HTC220-6-SO_3H.

Samples	HTC220-6	HTC220-6-SO_3H
BET surface area ($m^2\ g^{-1}$)	2.001	7.394
pore volume ($cm^3\ g^{-1}$)	0.006	0.005
Pore size (nm)	11.311	4.274
Total acidity (mmol g^{-1})	6.620	7.944
Sulfur content (mmol g^{-1})	–	0.709

3.3. Catalytic activities toward cellulose hydrolysis and fructose dehydration

HTC220-6-SO_3H was tested toward cellulose hydrolysis to monosaccharides in subcritical water at 180 °C for 5 min with 5 wt.% catalyst loading. The results were compared with non-catalytic condition and with different type of solid acid catalysts including HTC220-6, amberlyst 16 wet and GO at the same operating conditions. As shown in Fig. 3, the presence of solid acid catalysts clearly promotes the glucose product yield from the cellulose hydrolysis. The glucose yield from the reaction catalyzed by HTC220-6-SO_3H (43.63 ± 1.62 wt.%) was higher than that catalyzed by HTC220-6 (6.99 ± 0.11 wt.%), due to the higher acidity (as shown in Table 2). This clearly indicated the importance of SO_3H addition on the catalytic activity toward hydrolysis reaction. However, the results showed similar glucose yield in from the reaction in the presences of amberlyst 16 wet and GO (45.17 ± 0.35 wt.% and 41.71 ± 3.16 wt.%, respectively). Similar trends of byproduct yields including HMF and furfural were also observed. This indicated that HTC220-6-SO_3H exhibited the activity for sugar dehydration in the same range as amberlyst 16 wet and GO.

To confirm the catalytic activity of HTC220-6-SO_3H for dehydration, the solid acid catalysts were also tested in fructose dehydration (Fig. 4).The operating conditions was at 180 °C for 5 min without and with 5 wt.% catalyst loading. Without catalyst loading, the results revealed that the reaction achieved moderate fructose conversion (56.19 ± 2.86 wt.%) due to the possible self-dehydration of fructose under HCW condition. Daorattanachai et al. also reported high conversion (93%) of fructose under HCW at slightly higher temperature of

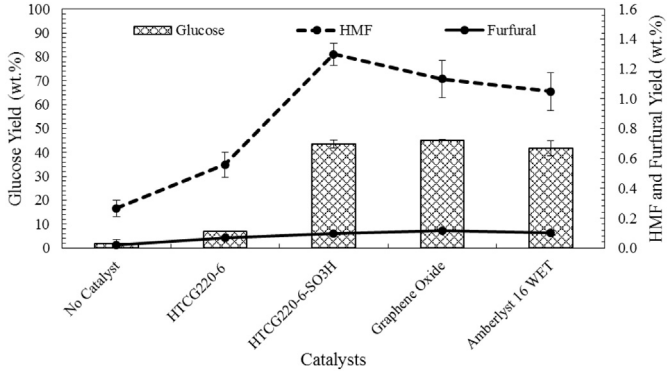

Fig. 3. Glucose, HMF, and furfural yields in liquid products of cellulose hydrolysis in subcritical water at 180 °C and 5 min and 5 wt.% catalyst loading, catalyzed by different catalysts.

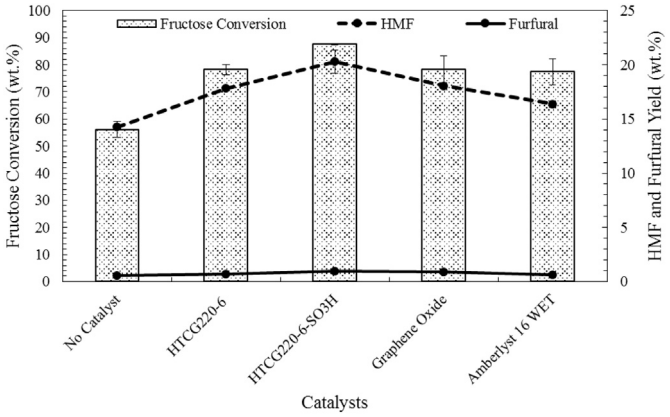

Fig. 4. Fructose conversion, HMF and furfural yields in liquid product of fructose dehydration in subcritical water at 180 °C and 5 min and 5 wt.% catalyst loading, catalyzed by different catalysts.

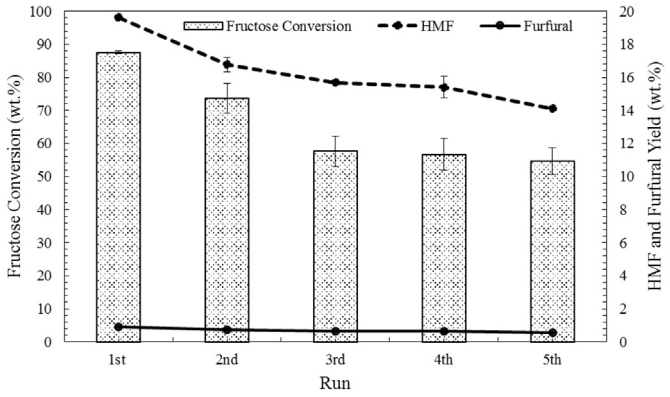

Fig. 5. Fructose conversion, HMF and furfural yields in liquid product of fructose dehydration in subcritical water at 180 °C and 5 min and 5 wt.% catalyst loading, catalyzed by recycled catalyst.

200 °C for 5 min without the presence of catalyst [35]. Among the catalysts used, HTC220-6-SO_3H exhibited the highest fructose dehydration activities, as suggested by the highest fructose conversion of 87.56 ± 0.37 wt.% and the correspondingly highest HMF and furfural yields of 20.29 ± 1.09 wt.% and 0.97 ± 0.05 wt.%, respectively. Moreover, HTC catalyst without sulfonation (HTC220-6) was found to have reasonable catalytic activity for fructose dehydration, and gave comparable HMF and furfural yields with amberlyst 16 wet and GO. It can be implied from the results that sulfonation process can improve the catalytic activities for cellulose hydrolysis and fructose dehydration. It should be noted that, previously, several solid catalysts have been tested toward the cellulose hydrolysis as summarized in Table S2. It can be seen that the catalyst in this study exhibited relatively higher glucose yield from the reaction (43.6%) than rare earth, metal, and metal-oxide based catalysts with less reaction time required (5 min). In addition, this catalyst also showed high fructose conversion (87.5%) with high HMF yield from the dehydration reaction compared to the previous reports [23]. Although sulfonation process was proved to be able to improve the catalytic activities, leaching of acid groups was also considered for acidic stability. From fructose dehydration test, the post-reaction sulfonated HTC was analyzed by FTIR. The resulted FTIR spectra exhibited similar FTIR characteristics to pure HTC, these indicating the leaching of $-SO_3H$ groups in HTC220-6-SO_3H after reaction.

Lastly, the recyclability of HTC220-6-SO_3H was also conducted toward fructose dehydration. As shown in Fig. 5, after 5 cycles, fructose conversion decreased from 87.56 ± 0.37 wt.% to 54.58 ± 4.09 wt.%, with the most rapid drop of reactivity observed in the second and the third reaction cycles, possibly due to leaching of acid groups from the catalyst. Similarly, the HMF yields decreased from 19.62 ± 0.14 wt.% to 14.11 ± 0.06 wt.% after 5 cycles, while no difference was observed in furfural yields, possibly due to very small amount of furfural in all reactions. This study therefore implied that acid leaching is the major concern of typical sulfonated catalysts and the development of catalyst that can minimize the acid leaching is further required.

4. Conclusions

HTC was successfully prepared by hydrothermal carbonization of glucose. The HTC samples prepared at different times and temperatures showed similar XRD crystallinity structures, functional groups and thermal stability. Nevertheless, the suitable hydrothermal carbonization conditions to prepare HTC as catalyst support for biomass conversion reaction was at 220 °C with the holding time > 6 h. After sulfonation, HTC220-6-SO_3H showed 20% increase in total acidity, and exhibited great catalytic activity toward cellulose hydrolysis and fructose dehydration reactions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2017.10.014.

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Sequential organosolv fractionation/hydrolysis of sugarcane bagasse: The coupling use of heterogeneous H_3PO_4-activated carbon as acid promoter and hydrolysis catalyst

Nopparat Suriyachai [a], Verawat Champreda [b, **], Chularat Sakdaronnarong [c], Artiwan Shotipruk [d], Navadol Laosiripojana [a, *]

[a] The Joint Graduate School for Energy and Environment (JGSEE), King Mongkut's University of Technology Thonburi, Prachauthit Road, Bangmod, Bangkok, 10140, Thailand
[b] Enzyme Technology Laboratory/ BIOTEC-JGSEE Integrative Biorefinery Laboratory, National Center for Genetic Engineering and Biotechnology, 113 Thailand Science Park, Phahonyothin Road, Khlong Luang, Pathumthani 12120, Thailand
[c] Department of Chemical Engineering, Faculty of Engineering, Mahidol University, 25/25 Phutthamonthon 4 Road, Salaya, Phutthamonthon, Nakorn Pathom, 73170, Thailand
[d] Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Thailand

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ABSTRACT

Separation of lignocellulose constituents and hydrolysis of the polysaccharides fraction to sugars are prerequites in production of biofuels and chemicals. In this study, a sequential organosolv fractionation of sugarcane bagasse and saccharification of the cellulose-enriched pulp in hot compressed water using a coupled heterogenous acid promoter/catalyst was studied. Among the liquid and solid acids tested, H_3PO_4-Activated carbon showed a high performance on promoting selectivity and yield in fractionation related to its high BET surface area and acid site density. Fractionation in a ternary mixture of methyl isolbutylketone:methanol:water (16:68:16) at 180 °C for 60 min using 5%w/w H_3PO_4-Activated carbon resulted in 88.9% recovery of cellulose enriched in the solid, together with 84.6% recovery of the hemicellulose as pentoses in the aqueous-alcohol fraction and 76.0% lignin in the organic phase. With no separation of the solid acid, the cellulose fraction could be further hydrolyzed under hot compressed water conditions at 225 °C for 10 min, resulting in the maximal hexose yield of 58.3% from the starting material. The catalyst retained >80% activity after reusing in five consecutive batch cycles. The work demonstrates an efficient integrated fractionation/hydrolysis process with coupling use of the acid promoter/catalyst, with advantages on its high activity, selectivity and reusability.

1. Introduction

Lignocellulosic biomass represents a promising renewable feedstock for production of fuels, chemicals, energy, and a variety of valuable co-products in biorefinery. Lignocellulose is a complex supra-molecular structure consisted mainly of three biopolymers: (i) Cellulose, a linear homopolymer of D-glucose linked by β-1,4-glycosidic linkages which forms into highly crystalline microfibers which are intimately linked to an intricate network of (ii) hemicellulose, a branched amorphous heterogenous polysaccharide comprising of pentoses (xylose and arabinose), hexoses (mannose, glucose, and galactose), and sugar acids and (iii) lignin, a heteropolymer comprising three different phenylpropane subunits, which shields the polysaccharide fraction from external environmental stresses and microbial attacks [1]. This complex and highly ordered structure makes lignocelluloses highly recalcitrant to degradation and subsequent conversion, which usually leads to high product variation with low selectivity.

Fractionation of lignocellulosic components is an initial step for value-added utilization of the individual biopolymers in integrated biorefineries producing multiple products [2]. The fractionation process entails disruption of lignocellulose biopolymeric matrix and subsequent separation of its components into isolated fractions

* Corresponding author.
** Corresponding author.
E-mail addresses: verawat@biotec.or.th (V. Champreda), navadol@jgsee.kmutt.ac.th (N. Laosiripojana).

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according to selectivity of the reaction media and process conditions [3]. An optimized fractionation process exhibits high selective separation of cellulose, hemicellulose, and lignin with high recovery yield and minimal purification requirement before further processing. Several fractionation methods based on chemical [4], hydrothermal [5], ionic liquid [6] or their combined [7] processes have been reported with variation in their efficiency and selectivity on different lignocellulosic materials. Among them, organosolv fractionation is a generally versatile process with respect to the raw materials. Ethanol and methanol are the most common solvents used for organosolv process, whereas several other alternative solvents have also been employed including organic bases, ketones, and esters [8–10]. Recently, the Clean Fractionation (CF) process using a ternary mixture of ketone, alcohol, and water in the presence of an acid promoter (i.e.H_2SO_4) has been introduced, allowing separation of high purity lignin in the organic phase and hemicellulose-derived products in the aqueous-alcohol fraction while leaving cellulose in the solid pulp [11]. This process has been later studied for modification of solvent systems and acid promoters and demonstrated for fractionation of lignocellulosic components in hardwood, softwood, and agricultural residues [12–14].

In sugar platform biorefinery, the polysaccharide fraction is initially hydrolyzed by chemical or enzymatic processes into sugars which can be further converted to a range of biofuels and commodity chemicals by catalytic or fermentation routes. Enzymatic hydrolysis has advantages on its high selectivity and mild operational conditions; nevertheless, the high cost and rapid deactivation of enzymes are the major challenges for industrial implementation [15,16]. Acid hydrolysis using mineral acids e.g. H_2SO_4, HCl, and H_3PO_4 also suffers from the corrosive nature of acids, formation of possible unwanted by-products, and the requirement for acid waste treatment [17]. Hot compressed water (HCW) has been proposed as a promising alternative for hydrolysis of lignocellulosic materials with advantages on environmental friendliness [18,19]. Under elevated temperature (160–240 °C) and pressurized conditions (5–20 bars), the superheated liquid water auto-ionizes into hydronium ions which act as a promoter for cleavage of ester bonds of acetyl side chains of hemicelluloses, which results in formation of acetic acid [20]. The *in situ* generated acid then autocatalyzes hydrolysis of the hemicellulose and alteration of lignin structure, leading to increased enzyme accessibility to the cellulose fibers. Addition of external acids and alkalis has been studied to increase the efficiency and selectivity of the hydrolysis reaction which led to lowering of the reaction temperature and hence, the energy requirement [21]. However, the use of homogenous catalysts leads to difficulties in catalyst recovery, product contamination, and solvent recycling as well as increasing cost on waste water treatment. Heterogeneous acid catalysts have been recently proposed for hydrolysis of lignocellulosic materials under HCW condition with the advantages on simple catalyst separation and recovery [22,23]. Among the currently developed solid acid catalysts e.g. zeolites, transition-metal oxides, cation-exchange resins, supported solid acids and heteropoly compounds, carbonaceous solid acids (CSA) have several favorable characteristics such as high catalytic activity and selectivity, long catalyst life, and ease in recovery. CSA catalysts with SO_3H, COOH and OH groups were studied for hydrolysis of cellulose and its derived polysaccharides [24–26].

In this study, application of CSA as a promoter on increasing efficiency and selectivity of a single-step CF-based organosolv fractionation of sugarcane bagasse was further studied from our previous work reporting the good properties of H_2SO_4- and H_3PO_4-Activated carbon on fractionation of woody biomass [13]. In addition, the coupling use of CSA for the sequential hydrolysis process was examined for combining the organosolv fractionation with the hydrothermal hydrolysis step without acid promoter removal required. The effects of reaction conditions on both steps were investigated to identify the optimum conditions for maximized sugar production. The novel developed process allows integration of the fractionation and the hydrolysis steps by the use of coupled acid catalyst.

2. Material and methods

2.1. Raw materials

Sugarcane bagasse was supplied from Phu Kiaew Bioenergy (Chaiyapoom, Thailand) and dried at 60 °C for 12 h. The biomass (initial size range of 1.5–2 cm) was physically processed using a cutting mill (Retsch SM2000, Hann, Germany) and sieved to obtain particles of diameter of 250–420 μm. The processed biomass was then used as starting material for experiments. Chemical compositions (percent lignin, cellulose, hemicelluloses, and ash) were analyzed using the standard NREL method [27]. The starting material contained 39.7 wt% cellulose, 28.0 wt% hemicellulose, 24.6 wt % lignin, 1.7 wt% ash and 5.5 wt% other contents. Activated carbon (total surface area 1343 m^2/g and average pore size 0.67 nm) was supplied from Carbokarn (Bangkok, Thailand), while analytical grade organic solvents and chemicals were purchased from major chemical suppliers i.e. Sigma-Aldrich, Merck, and Fluka.

2.2. Preparation of solid acid promoters

H_2SO_4- and H_3PO_4-Activated carbons were prepared from activated carbon with various functional acid groups (i.e. $H_2SO_4$and H_3PO_4). The experiment was carried out by mixing 10 g of activated carbon with 100 mL of the concentrated acid in a 250-mL 3-neck round bottom flask at 230 °C under flow of nitrogen (100 cm^3/min). A 1-L flask containing fresh activated carbon was connected to the reaction flask to adsorb the acid vapor through a condenser column (see schematic diagram in supplementary data). The nitrogen inlet flow was switched off when the reaction reached the desired temperature and the sample was further heated until the acid solution was completely evaporated. The obtained solid was repeatedly washed with boiling water until no pH change was observed in the filtrate (initial pH of 1 to final pH of 6) and used as the solid acid promoter as described in Suganuma et al. [25].

2.3. Procedure for fractionation

The fractionation process was modified from Bozell et al. [11]. Reactions were studied in a stainless steel reactor (1.27 cm diameter and 13 cm in length with the wall thickness of 10 mm) equipped with a thermocouple to measure the temperature inside the reactor. In the standard reaction, 1 g of bagasse and 6 mL of the single-phase solvent mixture comprising methyl isobutyl ketone (MIBK): methanol: water with the ratio of 16:68:16 (v/v) according to Klamrassamee et al. [13] or other solvents as indicated with and without the homogeneous (H_2SO_4 and H_3PO_4) or heterogeneous acid promoters (H_2SO_4- and H_3PO_4-activated carbons) in the reactor were heated to the desired temperature. Nitrogen was flowed into the reactor for purging and adjusting the initial pressure at 20 bars. The reactor was placed in a furnace and co-heated to 140–250 °C for 10–180 min. Uniform heating was achieved by the use of a relatively small reactor size. There was no noticeable difference between the temperature measured inside the reactor and the furnace temperature. After that, the reaction was immediately stopped by quenching in a water bath. The solid cellulose-enriched fraction was separated by filtration on filter paper and washed with MIBK (2 mL) then water (5 mL), and dried at 60 °C. The

liquid fraction was combined with the rinsate and placed into a separating funnel. Water was added to the aqueous-organic fraction until phase separation was obtained. The mixture was stirred and then placed at room temperature for 20 min for complete phase separation. The aqueous phase containing hemicellulose and soluble products was recovered. The separated organic phase was dried by evaporation at 105 °C to obtain lignin. Yields of isolated products in solid are reported as g of product in solid/100 g of raw material on a dried weight basis while their recovery yield are percentage of the individual component recovered from the starting material.

2.4. Procedure for HCW hydrolysis

The hydrolysis reaction was carried out in a stainless steel reactor (1.27 cm diameter and 13 cm in length) equipped with a thermocouple to measure temperature inside the reactor. The standard reaction contained 1 g of samples (i.e. fractionated bagasse) and 6 mL of water in the presence of H_2SO_4- and H_3PO_4-Activated carbons (1–10% w/w). Nitrogen was flowed into the reactor for purging and adjusting the initial pressure (5–20 bars). The reactor was placed in a furnace and heated to 100–250 °C for 5–40 min. The reaction was immediately stopped by quenching in a water bath. The solution was separated by a syringe filter (0.45 μm) for solid-liquid separation.

2.5. Characterization of promoters

The specific surface area, cumulative pore volume, and average pore diameter of solid acid promoter and solid catalysts were performed by N_2 physisorption technique using the Brunauer-Emmet-Teller (BET) method. Solid promoters and solid catalysts were analyzed for the BET surface area using a Belsorp-max TPD pro (BEL Japan, Tokyo, Japan) with thermal conductivity detector (Semi-diffusion type, 4-element W-Re filament). The acid-base properties of solid promoter and solid catalysts were analyzed by temperature-programmed desorption techniques (TPD) with ammonia and carbon dioxide (NH_3- and CO_2-TPD) [28]. In details, the samples (0.1 g) was heated at 500 °C in helium flow for 1 h and then saturated with 15% NH_3/He mixture or pure CO_2 flow after cooling to 100 °C. After purging with helium, the sample was heated to 650 °C under helium flow. The amount of acid-base sites on the catalyst surface was calculated from the desorption amount of NH_3 and CO_2. The areas of the desorption profiles were determined using the Chemisorption System analyzer (Micromeritics ChemiSorb 2750, Micromeritics Instrument Corp, Norcross, GA).

2.6. Liquid product analysis

Quantification and identification of liquid-products i.e.glucose, fructose, xylose, furfural, 3-hydroxylethylfurfural (HMF), and anhydroglucose (AHG) were conducted on a high performance liquid chromatograph equipped with a Dionex PDA-100 photodiode array detector with a Shodex RSpak KC-811 of 8.0 mm ID x 300 mm column. The possible product species included glucose, fructose, xylose, furfural, HMF, and AHG. The yield of each product was calculated by carbon balance, defined as the ratios of the amount of carbon atom in the specified product to the amount of carbon atom in the loaded feedstock.

2.7. Solid product analysis

For CHN analysis, the solid material was characterized by an Elemental Analyzer CHN-628 (LECO, St. Joseph, MI). The samples (0.1 g) was encapsulated in a tin container and operated under pure oxygen for complete combustion at 1050 °C in order to determine carbon (C), hydrogen (H), and nitrogen (N) content with Thermal Conductivity Detector (TCD).

Table 1
Surface area and porosity analysis of solid acid promoters.

Catalysts	BET surface area (m^2/g)	Cumulative pore volume (cm^3/g)	Average pore diameter (nm)
H_2SO_4-Activated carbon	801	0.47	1.72
H_3PO_4-Activated carbon	853	0.49	1.66

3. Results

3.1. Solid promoter characterization

Physicochemical characteristics of the synthesized solid acid promoters are summarized in Table 1. H_3PO_4-Activated carbon showed a specific surface area of 853 m^2/g which was higher than that of the sulfonated promoter (801 m^2/g) with a slightly higher cumulative pore volume but smaller pore size. It is noted that the pore size distribution of all samples are in the range of 0.4–1.3 nm. From TPD analyses, the phosphonated carbon contained higher acid site (1057.7 μmol/g) and density of acid site (1.24 μmol/m^2) compared with the sulfonated form according to the NH_3- and CO_2-TPD analysis (Fig. 1 and Table 2).

3.2. Fractionation of bagasse in the presence of different acid promoters

The fractionation process was initially studied at 180 °C for 60 min with the starting pressure at 20 bars in the absence or

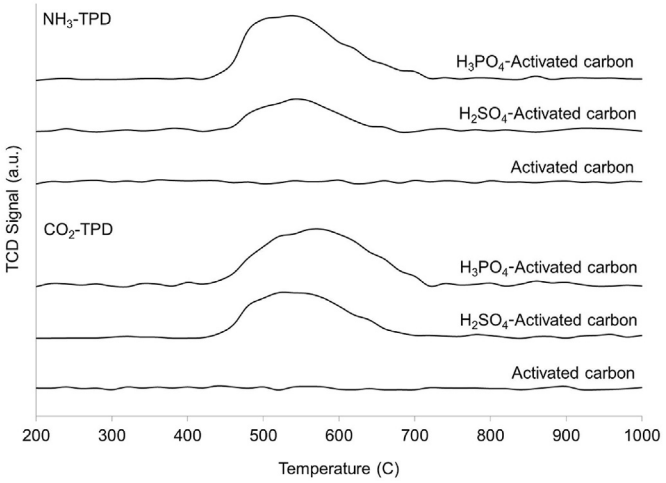

Fig. 1. TPD profiles of all acid promoters.

Table 2
Acid/base properties analysis of solid acid promoters.

Catalysts	Total sites (μmol/g)		Density of sites (μmol/m^2)	
	Acid sites[a]	Base sites[b]	Acid sites	Base sites
H_2SO_4-Activated carbon	873.1	344.4	1.09	0.43
H_3PO_4-Activated carbon	1057.7	307.1	1.24	0.36

[a] From NH_3-TPD.
[b] From CO_2-TPD.

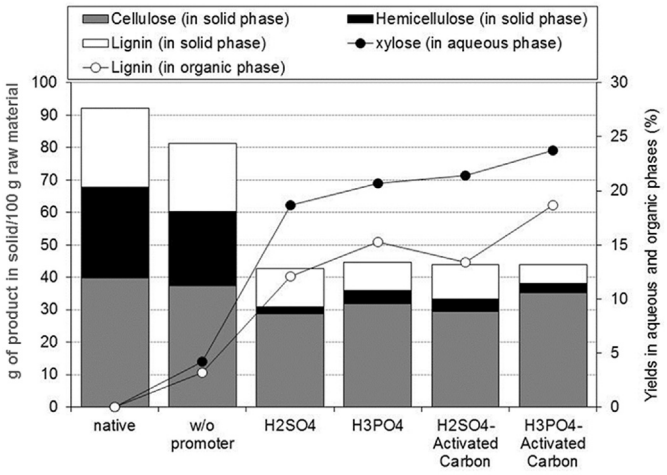

Fig. 2. Effects of homogeneous and heterogeneous acid promoter on the fractionation performance (MIBK: methanol: water of 16:68:16 at 180 °C for 60 min with the initial pressure of 20 bars). The data for the native biomass refers to composition of the raw material.

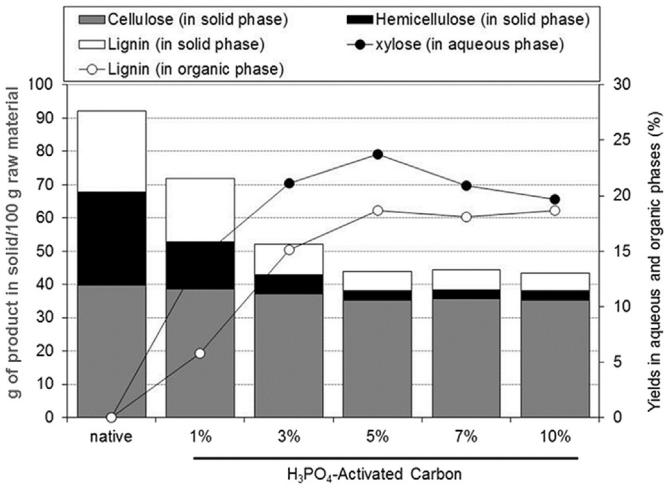

Fig. 3. Effects of H_3PO_4-activated carbon amount on the fractionation performance (MIBK: methanol: water of 16:68:16 at 180 °C for 60 min with the initial pressure of 20 bars). The data for the native biomass refers to composition of the raw material.

presence of 5% (w/w) acid promoters (homogeneous H_3PO_4 and H_2SO_4 and heterogeneous H_2SO_4- and H_3PO_4-Activated carbon). The initial ratio of the single-phase solvent mixture was at 16:68:16 (MIBK: methanol: water) based on volume. Fractionation under conditions with no acid promoter resulted in only slight decrease in composition of the solid fraction (37.4 g, 22.9 g, and 20.9 g/100 g raw material for cellulose, hemicellulose, and lignin, respectively), compared with the native biomass. Different solid promoters enhanced yield and selectivity of products from the fractionation process to a varying degree as shown by marked solubilization of hemicellulose and lignin from the solid biomass and hence, increasing of xylose-derived from hemicellulose hydrolysis in the aqueous phase and extracted lignin in the organic fraction. Among all types of promoters, H_3PO_4-Activated carbon gained the highest performance in terms of product yield and purity (Fig. 2). The solid fraction was highly enriched in cellulose (35.3 g/100 g raw material) with minor content of hemicellulose (2.9 g/100 g raw material) and lignin (5.6 g/100 g raw material) remained, while the aqueous phase contained the majority of hemicellulose fraction as xylose (23.7 g/100 g raw material) with slight cross-contamination by cellulose hydrolysis products (4.1 g/100 g raw material). A lignin yield of 18.7 g/100 g raw material was obtained in the organic phase with no cross-contamination of polysaccharide-derived products. The result therefore highlighted the potential use of H_3PO_4-Activated carbon as an acid promoter on the aqueous-organosolv fractionation process, from which good biomass fractionation performance could be achieved.

The effect of promoter amount on the fractionation performance was then studied by varying the weight of H_3PO_4-Activated carbon from 1 to 10% (w/w), while keeping other parameters constant. According to Fig. 3, addition of the promoter led to higher efficiency on removal of hemicellulose and lignin from the biomass. Further increase in promoter loading beyond 5% resulted in no substantial alteration in the solid composition and lignin yield obtained, while the xylose yield tended to decrease marginally. No marked decrease in the cellulose recovered was found in this range of promoter loading, suggesting high selectivity of the solid acid on the hemicellulose. This study revealed that the amount of acid promoter added played an important role on the fractionation efficiency as well as product distribution, from which the use of 5% w/w promoter gained the greatest fractionation performance.

3.3. Effects of fractionation conditions

The influence of reaction conditions on performance and selectivity of the fractionation process was studied by a one-at-a time optimization process. The effect of temperature on bagasse fractionation was studied by varying the reaction temperature while other operating conditions were kept constant (MIBK: methanol: water of 16:68:16 for 60 min with an initial pressure of 20 bars) in the presence of 5% H_3PO_4-Activated carbon. As shown in Fig. 4 (a) and (b), the total yield of xylose in aqueous phase increased sharply from 2.6 to 23.7%, whereas the lignin yield in organic phase substantially increased from 0.6 to 18.7 g/100 g raw material when the reaction temperature increased from 140 to 180 °C. The temperature increase also led to the production of glucose and cello-oligosaccharides from the hydrolysis of cellulose, which reflected in the decreasing trend of pulp yield. Further increase in temperature to above 200 °C led to decreases in the xylose and lignin yields with increase in the formation of side-products from sugar dehydration (furfural, HMF, and AHG). The optimal temperature was therefore suggested at 180 °C, from which the highest yields of xylose was obtained with slight cross-contamination of cellulose decomposed products in the aqueous phase with the remaining pulp yield of 64.8 wt%.

The effect of residence time was then investigated by varying the fractionation time from 10 min to 180 min while keeping the other parameters constant. As shown in Fig. 5, the soluble xylose and lignin yields increased rapidly with increasing in reaction time from 10 to 60 min. Further increases in fractionation time led to no substantial changes in pulp yield and composition of biopolymers in the pulp, whereas the xylose yield decreased due to its further decomposition to furans and organic acids via dehydration reaction. Therefore, the residence time of 60 min was suggested to be optimal for the reaction. It is noted that the effect of pressure was also examined by varying pressure from 5 bars to 30 bars; however, no substantial effect of pressure on the reaction performance was observed under the experimental conditions (Fig. 6).

3.4. Sequential fractionation/hydrolysis in the presence of H_3PO_4-Activated carbon

The sequential fractionation/hydrolysis process was further carried out under various operating conditions. The experiments

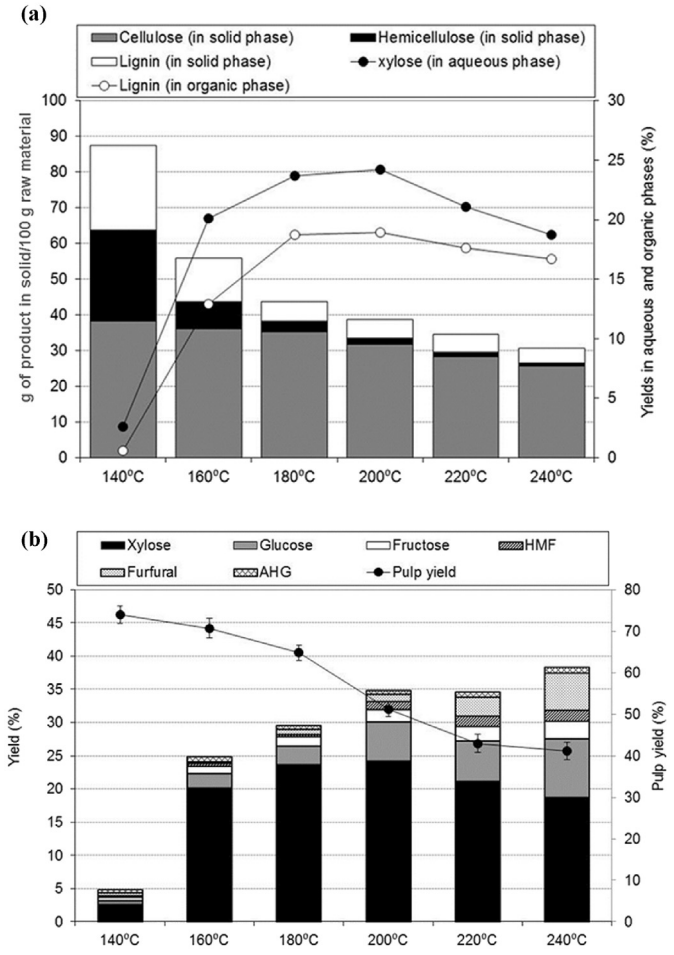

Fig. 4. Effects of temperature on the fractionation performance (a) and liquid product formation (b) (MIBK: methanol: water of 16:68:16 in the presence of 5% H_3PO_4-Activated carbon for 60 min with the initial pressure of 20 bars).

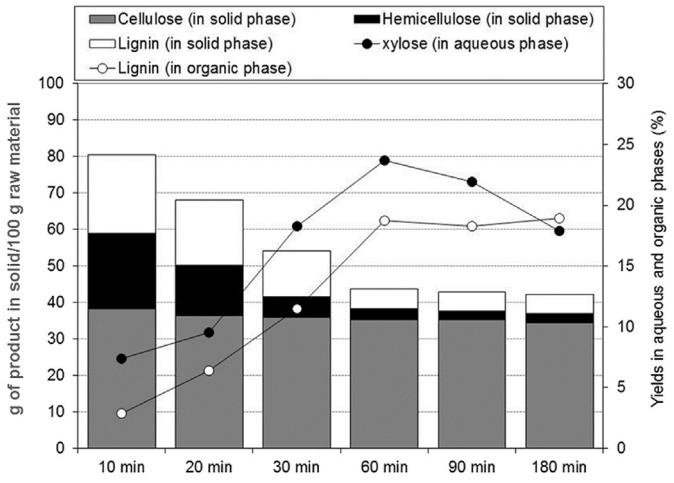

Fig. 5. Effects of reaction time on the fractionation performance (MIBK: methanol: water of 16:68:16 in the presence of 5% H_3PO_4-Activated carbon at 180 °C with the initial pressure of 20 bars).

were operated using the fractionated cellulose-enriched pulp from organosolv fractionation in the absence or presence of 5% H_3PO_4-Activated carbon. Initially, the reaction was carried out at 225 °C

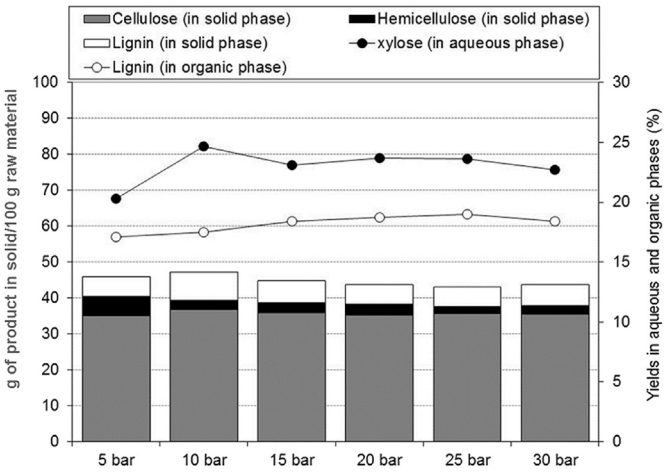

Fig. 6. Effects of initial pressure on the fractionation performance (MIBK: methanol: water of 16:68:16 in the presence of 5% H_3PO_4-Activated carbon at 180 °C for 60 min).

with the reaction time of 10 min. As shown in Fig. 7, the fractionated solid was more susceptible to hydrolysis compared to the native biomass under the hot compressed water conditions. Addition of 5% H_3PO_4-Activated carbon promoted hydrolysis of either the native biomass or the cellulose-enriched fraction, resulting in higher soluble products in the liquid phase. Glucose and fructose from glucose isomerization represented the two major products with xylose as a minor sugar with small cross contamination of sugar dehydration products. This finding highlights our achievement that, by integrating the fractionation with hydrolysis, a high proportion of xylose can be achieved from the fractionation step. Subsequently, from the sequential hydrolysis process, high purity glucose could be further obtained with a relative high yield (52%) based on the starting material, which could account up to nearly 60% yield when fructose was combined.

From the study, it is clear that H_3PO_4-Activated carbon can be efficiently used for both fractionation and hydrolysis without the removal step required. Furthermore, this integrative operation also highlights the great benefit in terms of higher sugar yield achievement and the capability to separate glucose and xylose in the final product. Further studies to optimize the hydrolysis activity of H_3PO_4-Activated carbon i.e. by varying reaction temperature and time, pressure were then carried out.

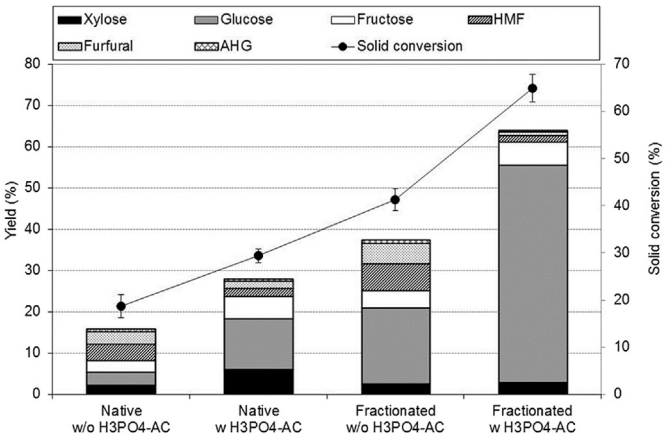

Fig. 7. Hydrolysis of native and fractionated bagasse with and without the presence of 5% H_3PO_4-activated carbon in pressurized liquid hot water at 225 °C with the reaction time of 10 min.

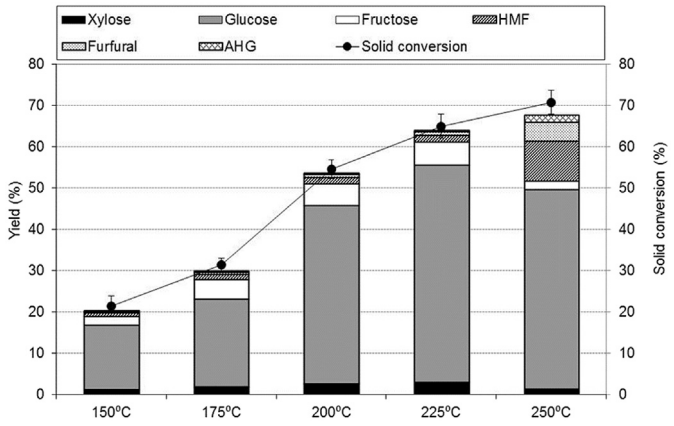

Fig. 8. Effects of temperature in pressurized liquid hot water on the hydrolysis performance of fractionated cellulose pulp in the presence of 5% H_3PO_4-Activated carbon with the reaction time of 10 min.

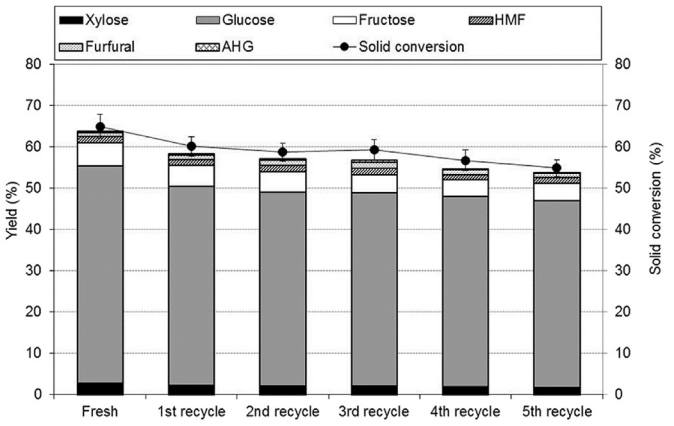

Fig. 10. Reusability testing of H_3PO_4-activated carbon for hydrolysis of fractionated bagasse in pressurized liquid hot water at 225 °C with the reaction time of 10 min.

3.5. Optimization of hydrolysis conditions

First, the effect of hydrolysis temperature on the product yield and the conversion of bagasse were examined over fractionated bagasse in the presence of H_3PO_4-Activated carbon an initial pressure of 20 bars and reaction time of 5 min. The effect of reaction temperature on the yields of liquid products is shown in Fig. 8. It can be seen that temperature showed marked effects on the feedstock conversion and yield of the liquid products. In details, the yield of sugar increased with increasing the reaction temperature from 150 °C to 225 °C; nevertheless, at the temperature above 225 °C, the yield of sugars and selectivity of the reaction decreased. In addition, significant formation of furans was detected at the temperature above 225 °C reflecting higher sugar dehydration rate at increasing reaction temperature from 200 °C to 250 °C. At the temperature between 150 and 225 °C, the rate of hydrolysis reaction was faster than the dehydration reaction, leading to accumulation sugars in the hydrolysis product. However, further increase in reaction temperature to 250 °C led to higher accumulation of HMF, furfural, and AHG. Hence, based on this result, the reaction temperature of 225 °C was the suitable temperature for the hydrolysis of bagasse.

In the next step, the effect of reaction time was studied by varying the holding time from 5 min to 40 min, while other operating conditions were kept constant. As shown in Fig. 9, it showed that the yield of sugars increased steadily with increasing the reaction time until 10 min before oppositely decreased with longer reaction time. The formation of furans (both HMF and furfural) markedly increased with longer reaction time. Therefore, the optimized condition for the hydrolysis of bagasse in the presence of H_3PO_4-Activated carbon was at 225 °C for 10 min, from which the highest sugars yield of 61.1% can be achieved (C_6 yield of 58.3% with small cross contamination of C_5 of 2.8%).

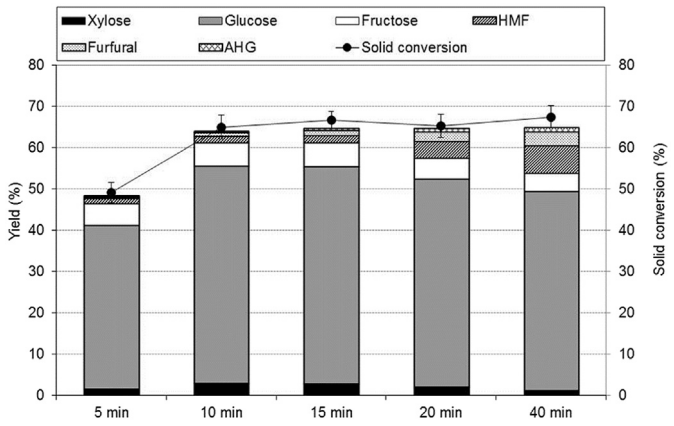

Fig. 9. Effects of reaction time on the hydrolysis performance of fractionated cellulose pulp in pressurized liquid hot water in the presence of 5% H_3PO_4-activated carbon with the reaction temperature of 225 °C.

3.6. Reusability of H_3PO_4-Activated carbon

The reusability of H_3PO_4-Activated carbon was studied by filtering it out from the remained solid residue after hydrolysis and reused for the hydrolysis processes. As shown in Fig. 10 and 8.9% decrease in hydrolysis efficiency was observed after the first batch; the hydrolysis performance then slightly changed from the 2^{nd}-5th batch recycling (with total 9.2% deactivation). It is noted that the reduction in efficiency could be due to partial leashing of acid under the experimental condition, according to the post-reaction NH_3- and CO_2-TPD measurements, from which the acidity reduced from 1057.7 μmol/g to 967.8, 938.4, 911.2, 895.5 and 879.1 μmol/g after 1^{st}-5th recycles, respectively.

4. Discussion

Fractionation of the primary lignocellulosic biopolymers with high yield and selectivity is a prerequisite step for maximization of biomass utilization in an integrated biorefinery process. Cellulose-enriched fraction provides the major homogenous source of glucose for conversion to biofuels (i.e.ethanol and higher alcohols) while hemicellulose fraction can be efficiently converted to fuels and a wide range of commodity chemicals by several catalytic and fermentation routes [29]. Lignin is currently used in boilers for heat generation; however, its utilization as composite materials or as a feedstock for conversion phenolic compounds are promising [30]. A recently reported Clean Fractionation (CF) technology allows efficient one-step separation of lignocellulosic, from which the use of a ternary solvent mixture has been reported to enhance lignin solubilization and retain its re-deposition on the cellulose solid pulp. The solvent ratio was initially designed based on the phase diagram modified from Bozell et al. [11] for preparation of an initially miscible mixture, which can then be disturbed by addition of water to result in an aqueous phase containing the hemicellulose-derived products, an organic phase containing lignin and the solid containing enriched cellulose according to their solubility

characteristics. The CF process has been previously optimized for separation of woody feedstocks, grasses and agricultural residues, particularly on various hardwoods e.g., aspen, poplar, and oak, focusing on yield and purity. The optimal process carried out in the presence of 0.1 M H_2SO_4 or greater led to a cellulose-enriched fraction with an average yield of 47.7 wt% containing Klason lignin of 5.1–6.8 wt% and trace amounts of cross-contaminating non-glucose sugars from woody biomass [11]. A glucan content in the solid pulp from batch separation could be greatly improved to over 89.9% under a flow-through condition. High-purity lignin was obtained with an average yield of 17.8–19.5 g/100 g raw material. The hemicelluloses fraction obtained was 14.5 g/100 g raw material in average and comprised a complex mixture of monomeric sugar e.g., xylose, mannose, uronic acids, and small amount of galactose and arabinose with dehydration products [11].

The fractionation using AC-H_3PO_4 reported in this study showed good performance and high selectivity compared to the previous works using conventional homogenous acids. The reaction medium and conditions optimized in our work was substantially different from that previously reported i.e. MIBK:MtOH:H_2O(16:68:16) compared to MIBK:EtOH:H_2O (16:34:50) [11], which was reported as the optimal ratio for various hardwoods under batch and flow-through conditions. The highly cellulose-enriched solid fraction of 80.6% homogeneity was obtained in this study with the typical yield of 35.3 g/100 g raw material, equivalent to 88.9% recovery of cellulose from the starting material. Typically, 23.7 g/100 g raw material hemicelluloses was recovered as soluble oligomeric and monomeric sugar products in the aqueous fraction with small molecular products e.g. organic acids, while 18.7 g/100 g raw material lignin was efficiently extracted and recovered in the organic phase with no significant sugar cross-contamination. These were equivalent to 84.6% and 76.0% recoveries of hemicellulose and lignin from the native biomass. The recovery yields of these major lignocellulosic components obtained in this study was relatively high compared to the previous work using the CF-fractionation processes using homogenous and solid acids on different biomass feedstocks [12–14] as well as other sequential separation processes using hydrothermal and chemical methods [31–33]. The decrease of monomeric and oligomeric sugar products at high temperatures could be due to their dehydration to furans and derivatives in the presence of mineral acids [19]. It should be noted that the hydrolysis of hemicellulose in the ternary solvent mixture started at 160 °C while partial cellulose decomposition started at 180 °C in the presence of acid promoter, which occurred at a lower temperature compared to that reported for non-catalytic hot compressed water [34]. The presence of acid promoters also showed strong effects on selectivity, separation effectiveness, and component yield from the fractionation process. Increasing acid concentration tended to result in higher levels of extracted lignin and hydrolysis of hemicelluloses, resulting in respectively higher purity of the pulp fraction, but with decreased pulp yield due to non-specific hydrolysis of the cellulose fraction. A typical barrier for commercial-scale application of homogeneous promoter, particularly a strong acid like H_2SO_4, is the problem on acid recovery and waste treatment. Furthermore, it is well established that the use of homogeneous acid compound is generally energy inefficient and leads to degradation of sugar monomers to inhibitory by-products in the subsequent fermentation step (e.g. furfural and HMF) and equipment corrosion. Development of solid heterogenous acid promoters as demonstrated in this study provides a promising way to overcome these problems; nevertheless, there are still limitations due to the catalyst deactivation, which comes from the leaching of acid from the surface of activated carbon after several recycles.

Regarding the use of acid promoter as hydrolysis catalyst, Tamtiengtrong et al. [29] previously reported the good hydrolysis activities of sulphonated activated carbon (AC-H_2SO_4)/phosphonated activated carbon (AC-H_3PO_4)/nitrated activated carbon (AC-HNO_3)/and hydrochorated activated carbon (AC-HCl) on eucalyptus, from which the highest sugars yield can be obtained by applying the H_3PO_4-activated carbon as the catalyst. These results are in good agreement with this study; however, with lower sugar yields (22%) compared to that achieved in our work. It has been indicated that solid acid catalysts have several favorable characteristics to replace homogeneous acid catalysts (i.e.H_2SO_4, HCl, H_3PO_4) for hydrolysis reaction such as high activity, high selectivity, long catalyst life and ease in recovery and reuse. Recently, Van de Vyveret al. 2011 [22] studied the conversion of cellulose using solid acid chemocatalysts catalysts and summarized their performance on sugar production. It was revealed that the carbonaceous solid acid (CSA) catalysts are considered as the most promising catalyst for cellulose hydrolysis, since they provide good access of reactants to the acidic sites of SO_3H and PO_3H_2 groups. The mechanism of lignocellulosic biomass hydrolysis with CSA catalysts is similar to that of homogeneous acids, from which protons in SO_3H and PO_3H_2 attack the β-1,4 glycosidic bonds in the solid crystalline cellulose. This is attributed to an increase in acidity of SO_3H and PO_3H_2 groups on the carbon material with a decrease in the amount of water.

5. Conclusions

From the study, H_3PO_4-Activated carbon was shown as an efficient promoter/catalyst for coupling of fractionation and hydrolysis without the removal required. This integrative operation also highlights the great benefit in terms of high biopolymer yields and purities from the fractionation step and higher sugar yield achievement from the hydrolysis step with the capability to separate glucose and xylose in the final product. The work demonstrated a novel sequential process for efficient processing of lignocellulosic feedstock for maximizing value of the biopolymers to multiple products in integrated biorefinery.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.renene.2017.06.003.

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The Effect of Pulsed Microwave Power on Transesterification of *Chlorella* sp. for Biodiesel Production

CHATTIP PROMMUAK[1], ISSARA SEREEWATTHANAWUT[2], PRASERT PAVASANT[1], ARMANDO T. QUITAIN[3], MOTONOBU GOTO[4], and ARTIWAN SHOTIPRUK[1]

[1]*Department of Chemical Engineering, Faculty of Engineering, Chemical Engineering Research Unit for Value Adding of Bioresources, Chulalongkorn University, Patumwan, Bangkok, Thailand*
[2]*Faculty of Engineering, Bangkokthonburi University, Taweewatana, Bangkok, Thailand*
[3]*Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, Kumamoto, Japan*
[4]*Department of Chemical Engineering, Graduate School of Engineering, Nagoya University, Nagoya, Japan*

Pulsed microwave technique was employed for the production of biodiesel from *Chlorella*sp. via transesterification. Real-time microwave power and temperature profiles were used for the evaluation of efficiency of biodiesel production. The effect of power setting was determined in the range of 100–1000 W at the fixed reaction time (10 min) and temperature (60°C). In this work, the highest yield of biodiesel per unit energy consumption observed was 0.53% by weight of crude lipid per kilo joule at 250 W. From the results in this study, the efficiency of biodiesel production was correlated to the uniform pulse intensity and pulse frequency during the reaction process provided at the power setting of 250 W.

Keywords: Biodiesel; *Chlorella*; Microalgae; Microwave; Transesterification

Introduction

Presently, microalgae are considered to be one of the most interesting raw materials for the production of biodiesel (Chisti, 2008; Atabani et al., 2012; McConnell and Farag, 2013). Due to its high lipid content, rapid growth rate, and less demand for cultivation land area compared with traditional sources like oil crops, this microorganism is believed to be the primary candidate for biodiesel production substituting the depleting fossil fuels (Atabani et al., 2012). However, the production of algal biodiesel has not yet been practical on industrial scale, as it requires high energy input (Ferrell and Sarisky-Reed, 2010). In contrast to crop seeds where a mechanical press process is generally applied, recovery of lipid from microalgae requires solvent extraction and energy-intensive recovery processes. The energy consumption in typical industrial applications contributes to more than half of the total production costs of biodiesel (Delrue et al., 2012).

Johnson and Wen (2009) and Elmoraghy and Farag (2014) proposed to combine the steps of extraction and chemical reaction into a single step for biodiesel production. That is, algal biomass, catalyst, and alcohol, which act both as an extractant and a reactant, are introduced into the system where the two processes occur simultaneously. The yield of biodiesel from the combined process was found to be comparable to that obtained from the traditional method. The production time was reduced by half and the operating cost was expected to be considerably lower.

In order to increase the rate of production of biodiesel from microalgae in the single-step process, microwave irradiation can be used as the heat source in place of conventional conduction heating. Koberg et al. (2011) reveals that direct transesterification of algal biomass under microwave irradiation provided nearly 100% conversion in 5 min in contrast to the 75% conversion obtained from a regular reflux system under the same operating conditions. The enhanced reaction rate could be a result of cell wall rupturing caused by microwave, leading to facilitated lipid extraction (Lee et al., 2010; Prommuak et al., 2012; Balasubramanian et al., 2011) as well as its effect on acceleration of chemical reactions (Jacob et al., 1995).

A number of studies have recently been conducted on microwave-assisted transesterification, particularly to determine the effects of various reaction conditions such as temperature, irradiation time, methanol (MeOH)-to-oil or to-biomass ratio, and the amount of catalyst on the biodiesel yield obtained from various sources including seed oil and algal lipid (Zhang et al., 2010; Hsiao et al., 2011; Patil et al., 2011). In addition to the aforementioned parameters,

Address correspondence to A. Shotipruk, Department of Chemical Engineering, Faculty of Engineering, Chemical Engineering Research Unit for Value Adding of Bioresources, Chulalongkorn University, Patumwan, Bangkok 10330, Thailand. E-mail: artiwan.sh@chula.ac.th

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microwave power has also been found to be one of the key factors affecting the reaction yield (Zu et al., 2009; Chen et al., 2012; Khemthong et al., 2012).

Due to their abundant availability, simple household and/or modified microwave systems were usually employed in most studies (Chen et al., 2012; Khemthong et al., 2012; Perin et al., 2008; Lertsathapornsuk et al., 2008). Limitation of such systems is that the typical low-cost magnetrons employed in these systems cause microwave field to be non-homogeneous. Furthermore, the simplicity of the controlling system in most commercially available microwave equipment does not allow the fine-tuning of the power input to a desired pattern resulting in non-isothermic conditions of the experiments. It is therefore not possible to conduct a consistent heating schedule and temperature control in such system.

Recently, specially designed microwave systems with built-in direct temperature control of the reaction mixture were developed. These microwave systems utilize fiber optic probes or infrared (IR) sensors and computer software to enable real-time control of temperature, pressure, and other process parameters by adjusting the pulsed microwave power output. These systems allow accurate control of power to the load as well as the heating rate (Kappe, 2004). Kim et al. (2011) employed this type of microwave system and demonstrated that esterification of oleic acid irradiated with pulsed microwave resulted in approximately 60% higher yield of methyl oleate than the one conducted under continuous microwave irradiation, with equal reaction time of 30 min.

The aim of this study was to determine the effect of pulsed microwave power settings on the biodiesel production yield from the biomass of *Chlorella* sp. The pulsed microwave system equipped with software for monitoring and recording real-time temperature and power profiles was employed. This system would allow accurate evaluation of the efficiency of the process, that is, yield of biodiesel per unit energy consumed.

Materials and Methods

Biomass and Sample Preparation

The liquid culture of *Chlorella* sp. containing 7% crude lipid by weight of algae was purchased from Pathumthani Inland Fisheries Research and Development Center, Pathumthani, Thailand. The sample contained 36% FFA by weight of crude lipid and the profile of the lipid was 20.2% linolenic acid, 13.1% palmitic acid, 10.7% linolenic acid, 2.4% oleic acid, and 0.3% stearic acid. Alga paste was obtained by dewatering the liquid culture in a continuous-flow centrifuge (a disk centrifuge, Alfa Laval DX203B-34, Spain), at 8000 rpm. The paste was then lyophilyzed to yield dry powder with the average size of 3 μm at − 40°C for 24 h. The lyophilized temperature and time were selected through dry-weight analysis method (i.e., no weight change was observed after lyophiliyzing at such conditions). All samples were stored at 4°C until their use.

Microwave-Assisted Biodiesel Production

The microwave-assisted biodiesel production was investigated with the apparatus, as shown in Figure 1. The apparatus

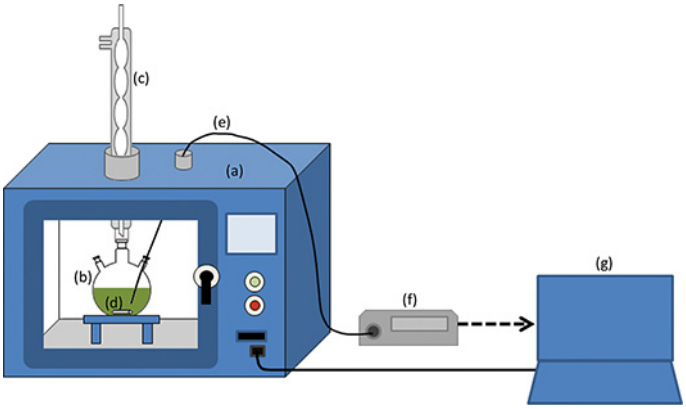

Fig. 1. Schematic diagram of pulsed microwave apparatus for biodiesel production.

(Shikoku Instrumentation Co., Ltd., Japan) consists of a microwave oven (a, Figure 1) generating magnetron with a frequency of 2.45 GHz and the wavelength of 122 mm. The system used in this work is a multimode system which employed the mode stirrer allowing the microwave to randomly distribute in the cavity, reducing the effect of non-uniform heat distribution. The experiment was conducted by charging 72 ml of 99% MeOH and 0.48 ml of 98% H_2SO_4 (both from Wako Pure Chemical Industries) into a round glass flask (b, Figure 1) containing 3 g of algal biomass. It is noted that acid (H_2SO_4) was selected in this study to avoid possible saponification of FFAs as found with alkali-based catalyst (i.e., KOH). In this work, excess amount of MeOH was used as it served as both reactant and extracting solvent. The flask was equipped with a condenser (c, Figure 1) with cooling water (2–4°C) circulating to maintain the volume of the liquid in the system. A magnetic stirrer (d, Figure 1) was put into the flask and was stirred at 300 rpm. With a fiber optic sensor (e, Figure 1) connected to a meter (f, Figure 1), the reaction temperature was monitored. The reaction temperature was maintained at 60°C by automatic adjustment of the microwave power.

The reaction time began as soon as the set point temperature (60°C) was attained. Transesterification was then allowed to take place for 10 min, after which the reaction mixture was cooled down to the room temperature. Algal cells were filtered out of the reaction mixture using filter paper Whatman No.5 (retention 2.5 μm). Chloroform and water were then added to the permeate at the ratio of 10:10:9 (permeate:chloroform:water) for further separation. The permeate−chloroform−water mixture was then centrifuged for 10 min at 2000 rpm, resulting in separation into two phases. MeOH and other polar impurities dissolved in water, which formed the upper phase, while fatty acid methyl esters (FAME), free fatty acids (FFA), and other neutral lipids dissolved in the chloroform occupied the bottom phase. The latter was then analyzed for FAMEs content using gas chromatography (GC). In this study, the effect of power settings at 100, 250, 500, 750, and 1000 W were investigated. For all power settings, microwave energy was supplied in a pulse mode with a duty cycle of 20%. The

software (SLP-C35, Yamatake Corp, Japan) was used to report the real-time profiles of microwave power and reaction temperature. The energy consumption for all experimental conditions was calculated by integrating the areas under the power−time series profiles.

GC Analysis for Biodiesel

The analysis for the amounts of FAMEs in the chloroform fraction was carried out using GC (Shimadzu GC-14B), equipped with a flame ionization detector (FID) with an injection volume of 0.1 µl. The separation of the sample products was achieved using a capillary column (CP-FFAP CB, 25 m (length), 0.32 mm (ID), 0.3 µm (film thickness), Varian, California). The injector and detector temperatures were set at 270°C and 300°C, respectively. The elution temperature program started with an initial temperature of 100°C which was held for 5 min prior to linear ramping with the rate of 10°C/min to the final temperature of 250°C. The final temperature was then held for 20 min, resulting in a total run time of 40 min. The concentration of biodiesel was quantified and the mass of biodiesel was calculated based on standard mixture of 5 FAMEs found in most biodiesels including palmitic, stearic, oleic, linoleic, and linolenic acid methyl ester (Wako, Japan). The yield of biodiesel in this study was further calculated as the percentage of total weight of these five FAMEs divided by the weight of crude lipid. For the analysis, heptadecanoic acid methyl ester (Wako) was used as an internal standard.

Results and Discussion

Microwave Power and Temperature Profiles

As shown in Figure 2, for all power settings, the profiles of microwave power and temperature can be divided into two periods: the ramping period and the holding period. In the first period, microwave supplied the maximum power until the desired temperature (60°C) was attained. Subsequently, in the second period, the system supplied only sufficient power to maintain the set temperature. It can also be seen from Figure 2 that with the power setting of 100 W, the

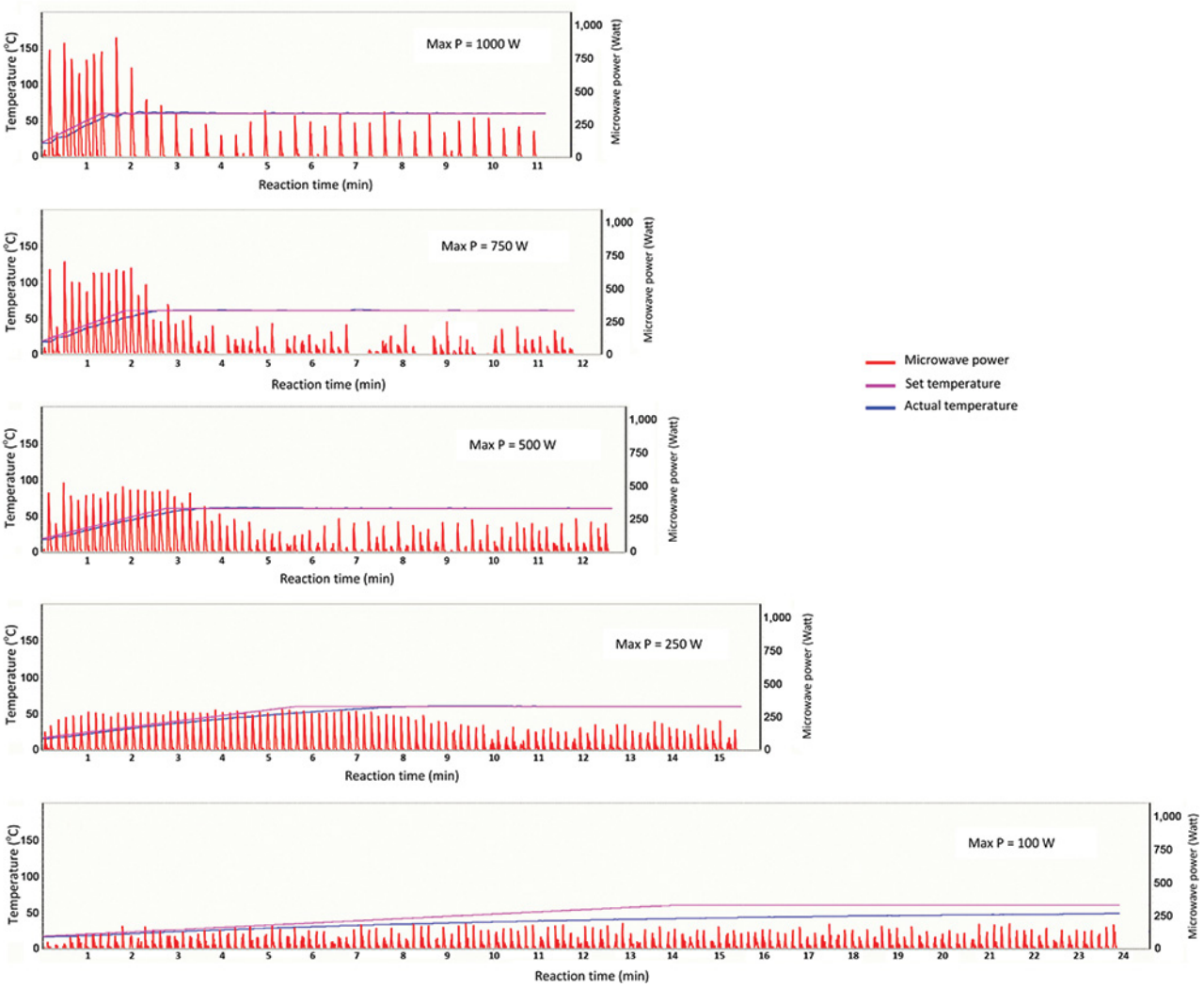

Fig. 2. Microwave power and temperature profiles at each maximum power setting of 100–1000 W.

Table I. Pulse frequency at various maximum microwave power settings

Max power (W)	Number of pulses/min (frequency)	
	Ramping	Holding at 60°C
100	6.2	6.0
250	6.4	5.9
500	6.3	5.9
750	6.7	5.2
1000	6.9	2.9

system could not reach the desired temperature of 60°C (only 35°C was attained). As the maximum power was adjusted to higher levels, the time to reach the set temperature for the reaction system became considerably shorter. In addition, it should be noted that not only the peak intensities were lower during the holding period but the pulse frequencies (the numbers of pulses per minute) also became smaller, despite the set duty cycle of 20%. The pulse frequencies during the ramping and holding periods at various power settings are summarized in Table 1. It can be seen from this table and also from the power profiles in Figure 2 that at lower maximum power settings (≤500 W), the power levels and pulse frequencies did not differ considerably between the ramping and the holding periods. As the maximum power settings increased further (750 and 1000 W), the power levels as well as the pulse frequencies differ significantly between the two periods.

Effect of Power Setting on FAMEs Yield

The FAMEs yields obtained from the reaction under various microwave power levels (at 60°C and 10 min holding time) are summarized in Table 2. The highest FAMEs yield of 24.3% was found at the power setting of 250 W. The yield was, however, comparable to that obtained for the reaction irradiated by pulsed microwave at 100 W despite that at this condition the set temperature 60°C could not be reached. The reason for rather high yields at 100 W was probably due to the extended heating (ramping) time (13.8 min) during which the reaction was continuously taking place although at a lower temperature. Since the start-up time differed for each experiment, the FAMEs yields are also considered in terms of yield per unit of total time. It can be seen that the FAMEs yield per unit of total time (ramping time + time the reaction was held at 60°C) was the lowest for the power setting of 100 W as well as at 1000 W. Thus, these conditions are not recommended as a suitable power setting. In this work, FAMEs yield per unit time is the highest for the power setting of 500 W, followed by that at 250 W. Alternative to FAMEs yields per unit time, the efficiency of the reaction could be determined based on the amount of energy used to produce a fixed amount of biodiesel. Integration of peak area gives the energy supplied by the microwave to the reaction system. FAMEs yield per unit energy could then be determined and the results are summarized in the last column of Table 2. This FAMEs yield

Table II. FAMEs yield and energy consumption for each maximum microwave power setting

Max power (W)	Duration (min)			FAME yield[b] (% by weight of crude lipid)	FAME yield per unit time[b/a] (% by weight of crude lipid/min)	Energy Consumption (kJ)			Energy Consumption per unit time[c/a] (kJ/min)	FAME yield per unit energy (% by weight of crude lipid/kJ)[b/c]
	Ramping	Hold at 60°C	Total[a]			Ramping	Hold at 60°C	Total[c]		
100	13.8	10	23.8	23 ± 0.7	0.97	35.3	26.5	61.8	2.6	0.37
250	5.5	10	15.5	24.3 ± 2.3	1.57	23.3	22.2	45.5	2.9	0.53
500	2.7	10	12.7	20.6 ± 0.7	1.62	26.1	37.3	63.4	5.0	0.32
750	1.8	10	11.8	15.3 ± 2.0	1.30	24.9	33.1	58.0	4.9	0.26
1000	1.3	10	11.3	11 ± 0.1	0.97	21.2	36.5	57.7	5.1	0.19

per unit energy was the highest when the maximum power setting of pulsed microwave was 250 W, suggesting that the reaction occurs most efficiently at this power setting. Except for 100 W, the yield per unit energy values seem to decrease with increasing power indicating lower efficiencies at higher power settings.

Based on these observations and the pulse data from previous section (Figure 2 and Table 1), higher yields seem to correlate well with uniform pulse frequencies as in the cases of 100 W and 250 W. When a higher power setting was used, the system automatically adjusted the pulse rate despite the set 20% cycle, and when the pulse frequency was further reduced as in the case of 1000 W, considerably lower yield was resulted. This result may be supported by the study by Asakuma et al. (2011) in which the nonthermal effect of microwave on transesterification of triglyceride has been described. That is, when exposed to microwave radiation, molecules of tri-glyceride try to align themselves with the rotating magnetic fields. The molecules collide with each other and cause not only friction heating, but also isomerization of the molecules to different forms. The resulting isomers were demonstrated to have lower dipole moment, which resulted in less activation energy when transesterified to FAMEs and thus the reaction occurred rapidly. Nevertheless, the molecules remained in this form only momentarily and reverted back to the original form without applied microwave irradiation. Hence, frequent pulse numbers per unit time is preferable to allow the isomer to stay activated. As seen from Figure 2 (except the data at 100 W for which the set temperature could not be achieved), at the power setting of 250 W where the pulse frequency was most uniform and the difference in peak intensities between the ramping and the holding period was minimal, the FAMEs yield per unit energy was the highest. This result seems to contradict with that reported by Kim et al. (2011), which suggested that pulsed microwave with higher power setting but lower duty cycle would result in greater biodiesel yield. The differences in findings could be due to the differences in the reaction system and the microwave systems that were used. The pulsed period in the system employed by Kim et al. (2011) was much shorter (in microseconds) than that of the system used in the present study. Therefore, the molecules may still stay isomerized even when irradiated with high-intensity pulses at lower duty cycle.

Conclusions

Production of biodiesel from *Chlorella* sp. under pulsed microwave irradiation was found to be greatly affected by the pulsing characteristic, which in turn depends on the power setting of the system. Based on the results in this study, higher algal FAMEs yield was obtained when the power was set to the lower levels, where the pulses appeared to have lower intensities but higher and more uniform frequencies. At these lower power settings, energy consumption per unit biodiesel production was lower compared with that resulted at higher power settings. The results reported in this work provide a promising outcome of biodiesel production using pulsed microwave technique. By adjusting the power setting, it is possible to improve the efficiency of the algal biodiesel production. Further study on physical and chemical mechanism of the reactions as well as energy efficiency analysis in comparison to conventional production processes can be conducted to evaluate the feasibility of the process development at commercial scale.

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Hydrolysis of eucalyptus wood chips under hot compressed water in the presence of sulfonated carbon-based catalysts

Khatiya Weerasai[a], *Verawat Champreda*[b,c], *Chularat Sakdaronnarong*[d], *Artiwan Shotipruk*[e], *Navadol Laosiripojana*[a,c,*]

[a] *The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Prachauthit Road, Bangmod, Bangkok 10140, Thailand*
[b] *Enzyme Technology Laboratory, National Center for Genetic Engineering and Biotechnology, 113 Thailand Science Park, Pahonyothin Road, Khlong Luang, Patumthani 12120, Thailand*
[c] *JGSEE-BIOTEC Integrative Biorefinery Laboratory, National Center for Genetic Engineering and Biotechnology, 113 Thailand Science Park, Pahonyothin Road, Khlong Luang, Patumthani 12120, Thailand*
[d] *Department of Chemical Engineering, Faculty of Engineering, Mahidol University, 25/25 Phutthamonthon 4 Road, Salaya, Phutthamonthon, Nakorn Pathom 73170, Thailand*
[e] *Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Thailand*

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ABSTRACT

Hydrolysis of lignocellulosic biomass to sugars and derivatives is a key step in production of biofuels and commodity chemicals in a biorefinery. In this study, catalytic hydrolysis of eucalyptus chips with solid sulfonated carbon-based catalysts prepared from three different carbon precursors (sucrose, glucose, and xylose) was studied under hot-compressed water at 150–250 °C with reaction time of 1–10 min. Increasing temperature up to 200 °C led to higher sugar yields from cellulose and hemicellulose while further increase in temperature caused higher formation of sugar degradation by-products. Sulfonated-sucrose (SO_3H-Suc) showed the greatest performance on sugar production compared to other catalysts with less formation of furans and anhydroglucose; its high catalytic activity was related to its high acid site density as proven by NH_3-TPD measurement. Size reduction and chemical pretreatment of the biomass were found to enhance the hydrolysis yield and reaction selectivity. The highest sugar yield of 40.7% comprising glucose, fructose, and xylose was achieved using 5% (w/w) SO_3H-Suc at 200 °C for 5 min with milled biomass (60–100 μm) pretreated by alkaline oxidation. The work provides an alternative catalytic process for hydrolysis of lignocellulose in biomass industry.

1. Introduction

The conversion of renewable resources to fuels and chemicals has gained an increasing interest in recent years as a promising approach to reduce dependence on fossil fuel resources. Production of second generation liquid biofuels (e.g. bio-ethanol, bio-butanol and drop-in fuels) and platform chemicals from renewable lignocellulosic biomass is recognized as a potential sustainable industry for the coming decade (Lynd et al., 2002). Lignocellulose is a complex material, consisting of three major biopolymers i.e. cellulose, hemicelluloses, and

* *Corresponding author at*: The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Prachauthit Road, Bangmod, Bangkok 10140, Thailand.
E-mail address: navadol@jgsee.kmutt.ac.th (N. Laosiripojana).
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lignin, which are associated with each other in addition to small amounts of acids, salts, and minerals (Fengel and Wegener, 1984). Cellulose is a linear homopolymer of D-glucose which forms into highly organized microfibril structures. Hemicellulose is an amorphous branched heterogenous polysaccharide comprising pentoses, such as xylose and arabinose as the main components with some hexoses and sugar acids. It acts as linkages between cellulose fibers and lignin, a highly complex polymer consisted of three major phenolic units: *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, which shields the plant cell. This complex structure thus results in the highly recalcitrance nature of lignocellulose to chemical or enzymatic decomposition.

In a sugar platform biorefinery, lignocellulosic materials are initially hydrolyzed into monomeric sugars which are then further converted to target bio-products by catalytic or biological processes. Enzymatic hydrolysis has advantages on its high selectivity and mild operational conditions; nevertheless, the enzyme's cost and its deactivation in the presence of inhibitors from the prior chemical or thermal pretreatment step are still the challenge for industrial implementation (Brethauer and Wyman, 2010). Alternatively, acid hydrolysis using mineral acids e.g. H_2SO_4, HCl, and H_3PO can overcome these problems; however, the corrosive nature of strong acids, the higher formation of unwanted by-products, and the requirement of acid-containing waste treatment are the main concerns (Gamez et al., 2006; Karimi et al., 2006; Lenihan et al., 2010).

Hot compressed water (HCW) has been proposed for hydrolysis of lignocellulosic materials with advantages on environmental friendliness and simple reaction control through optimization of water density (Kruse and Dinjus, 2007; Fang and Fang, 2008; Carvalheiro et al., 2009). In HCW, water acts as the sole reaction medium at subcritical temperatures under high pressure conditions. Under these conditions, water molecules are ionized in situ to hydronium ions. This results in the release of acetic acid from side chains of hemicellulose which in turn auto-catalyzes the solubilization of hemicelluloses under the acidic environment (Teo et al., 2010). The main barrier for HCW hydrolysis technology is the requirement of high energy input, which could be partially reduced by the addition of external acid or alkali to help catalyze the reactions and control downstream decomposition of sugars to by-products e.g. furans and organic acids (Watanabe et al., 2005; Asghari and Yoshida, 2006). However, the use of conventional liquid catalysts has drawbacks in product separation, catalyst recovery and solvent recycling as well as increasing cost on waste water treatment. Heterogeneous solid acid catalysts have been investigated for hydrolysis of various lignocellulosic materials with key advantages on easy catalyst separation and recovery (Chareonlimkun et al., 2010; Van de Vyver et al., 2011; Ding et al., 2012; Tan et al., 2013). Several solid acid catalysts have been reported, for examples, zeolites, cation-exchange resins, transition metal oxides, carbonaceous solid acids (CSA), and supported solid acids and heteropoly compounds (Bootsma and Shanks, 2007; Takagaki et al., 2008; Kobayashi et al., 2010; Zhou et al., 2013) with differences in their catalytic activity, selectivity, and catalyst life. CSA catalysts with SO_3H, COOH and OH groups were studied for hydrolysis of cellulose and its derived polysaccharides (Onda et al., 2008; Suganuma et al., 2008; Kitano et al., 2009; Pang et al., 2010; Suganuma et al., 2010; Fukuhara et al., 2011).

In this research, the hydrolysis of eucalyptus under HCW was studied in the presence of sulfonated carbon-based catalysts prepared from different carbon precursors (i.e. sucrose, glucose, and xylose). It is noted that eucalyptus wood chip was chosen in the present study since it is a raw material commonly used in pulp mills and is considered as a highly potent alternative feedstock for sugar platform biorefinery. The catalyst performance was evaluated based on C_5 and C_6 sugar yields and reaction selectivity compared to the use of liquid H_2SO_4. The effects of reaction temperature and time were investigated to identify the optimum conditions for maximized sugar production. Effects of biomass size and chemical pretreatment prior to the catalytic hydrolysis were also demonstrated. The work provides the report on application of SO_3H CSA and the influence of carbon precursor on catalytic hydrolysis of real lignocellulosic materials.

2. Experimental

2.1. Materials

Eucalyptus (*Eucalyptus grandis*) wood chips were provided by a local pulp mill in Ratchaburi province, Thailand. It contained 45.2% cellulose, 21.1% hemicelluloses, 30.4% lignin, and 3.3% of ash and other contents according the standard NREL analysis method (Sluiter et al., 2008). The sample was firstly ground by ball-milling to 100–250 μm for catalyst screening and reaction optimization study or to the specified size ranges as indicated. The biomass was pretreated by alkaline delignification using 5% (w/v) NaOH at 90 °C for 20 min with the solid loading of 10% (w/v) or alkaline hydrogen peroxide pretreatment using 5% (w/v) H_2O_2 at pH 11.5, 45 °C for 24 h. It is noted that these pretreatment processes were chosen in this study since alkaline pretreatment is the conventional pretreatment process of eucalyptus wood chip in pulp mill, while alkaline hydrogen peroxide pretreatment is known to be highly effective at delignification and also applicable for large-scale application. The solid residues were washed with water to neutral pH and then dried at 100 °C. Cellulose (Avicel), xylan (Birch wood), all organic solvents and chemicals were analytical grade from major suppliers e.g. Sigma-Aldrich, Merck, and Fluka.

2.2. Preparation and characterization of carbon-based acid catalysts

The catalysts were prepared by adding 10 g of carbon materials (sucrose, glucose, and xylose) to 100 mL of concentrated H_2SO_4 in a 4-neck round bottom flask. The reaction mixture was heated at 250 °C under the flow of N_2 to produce a brown-black solid. A 1-L flask containing the solid sample was connected to the reaction flask to adsorb the acid vapor. The N_2 inlet flow was stopped when the reaction reached the target temperature. The sample was further heated to completely evaporate the acid solution. The obtained solid fraction was washed repeatedly with boiling water until the filtrate showed no pH change and used as the catalysts in this study. It is noted that the hydrothermal carbon (HTC) from these three sugars without H_2SO_4 additional was also synthesized and characterized for comparison.

The specific area and pore size of solid acid and HTC catalysts was analyzed by N_2 physisorption technique based on the Brunauer–Emmet–Teller (BET) method using a Belsorp-max TPD pro (BEL Japan, Tokyo, Japan) equipped with a thermal conductivity detector (Semi-diffusion type, 4-element W-Re filament). The acid–base properties were analyzed by temperature-programmed desorption technique (TPD) [NH_3-TPD] (Ding et al., 2012). In addition to BET and TPD analyses, a scanning electron microscope (SEM, JEOL, JSM-6610 LV) was used for the morphology observation of SO_3H-Suc compared to HTC (prepared from sucrose), while the functional groups on SO_3H-Suc and HTC (prepared from sucrose) were analyzed by Fourier-Transformed Infrared Spectroscopy (FT-IR) (Perkin-Elmer System 2000, Waltham, United States) with infrared spectra collected in the wave number range of 400–4000 cm^{-1}.

2.3. Study of hydrolysis reaction

The hydrolysis reaction was carried out in a stainless steel reactor (1.27 cm diameter and 13 cm in length) equipped with

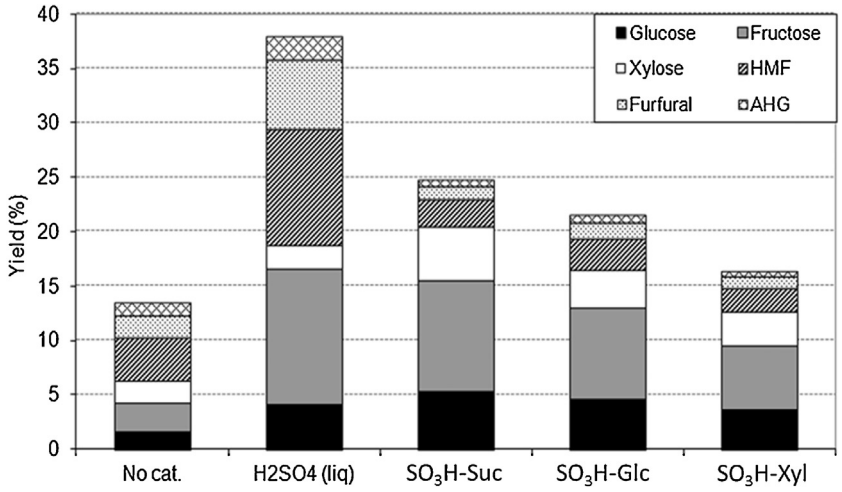

Fig. 1 – Effects of solid catalysts on yield of liquid products from hydrolysis of milled eucalyptus under HCW. Reactions (6 mL) contained 1 g biomass and were heated at 200 °C for 5 min with or without 5% SO_3H-based catalyst. H_2SO_4 with the equal acid content was studied for comparison.

a thermocouple to measure temperature in the reactor. The reaction contained 1 g of milled eucalyptus sample on a dried weight basis and 6 mL of water in the presence of heterogeneous acid catalysts (5% w/w of water) compared to that using an equal acid loading based on identical acidity (H_3O^+) of homologenous catalyst (H_2SO_4). Nitrogen was purged into the reactor for adjusting the initial pressure (5–20 bar). The reactor was placed in a furnace and heated at 100–250 °C for 5–40 min. The reaction was stopped by quenching in a water bath. The solution was separated by a syringe filter (0.45 μm) for solid–liquid separation.

2.4. *Analytical methods*

Quantification and identification of liquid-products i.e. glucose, fructose, xylose, furfural, 3-hydroxylethylfurfural (HMF), and anhydroglucose (AHG) were performed on a high performance liquid chromatograph system equipped with a Dionex PDA-100 photodiode array detector and a Shodex RSpak KC-811 column. The yield of each product was calculated by carbon balance, defined as the ratios of the amount of carbon atom in the specified product to the amount of carbon atom in the loaded feedstock. It is noted that the total amount of carbon in the recovered water solution was measured using the TOC (total organic carbon detector, Shimadzu, model TOC-5000 A).

3. Results and discussion

3.1. *Hydrolysis of eucalyptus under HCW condition*

The hydrolysis of eucalyptus using HCW was initially studied with and without the presence of synthesized sulfonated carbon-based catalysts (SO_3H-Suc, SO_3H-Glc, and SO_3H-Xyl). The reaction using liquid H_2SO_4 with the same acid content as the solid-acid catalysts was also tested for comparison. In this study, the reaction containing 1 g of eucalyptus in the presence of 0.05 g of catalyst in 6 mL of water was initially tested at 200 °C with the reaction time of 5 min. As presented in Fig. 1, the hydrolysis reaction resulted in the release of glucose and xylose from hydrolysis of cellulose and hemicellulose into the liquid phase. A substantial amount of glucose was isomerized into fructose under the experimental conditions

Table 1 – Surface area and acid properties of sulfonated carbon-based catalysts prepared on different carbon precursors.

Catalysts	BET surface area[a] (m^2/g)	Amount of acid site (μmol/g)	Density of acid site (μmol/m^2)
SO_3H-Suc	1.8	34.7	19.2
SO_3H-Glc	1.5	18.3	12.2
SO_3H-Xyl	1.5	16.5	11.0
HTC-Suc	1.3	12.4	9.5
HTC-Glc	1.2	11.8	9.1
HTC-Xyl	1.2	11.5	9.6

[a] Error of measurement = ±5%.

while side-products from sugar dehydration (furfural, HMF, and AHG) were found. SO_3H-Suc showed the highest catalyst performance on hydrolysis efficiency as shown by the highest sugar yield with the lowest relative HMF, furfural and AHG formations. This led to the C_6 sugar (glucose and fructose) yield of 15.5% and C_5 sugar (xylose) yield of 4.9% with 4.3% yield for the side-products. Slightly higher C_6 sugar yield (16.6%) was obtained using liquid H_2SO_4; however, with a lower C_5 sugar yield. A marked increase in formation of the side products (19.1%) were observed using H_2SO_4 due to the strong promotion of dehydration reaction, suggesting higher reaction selectivity of the solid catalysts toward sugar production. The reaction with no catalyst showed noticeably lower sugar yields (6.2%) with relatively high furfural and HMF formations (7.2%).

All BET and TPD analyses are presented in Table 1. It can be seen that SO_3H-Suc presents relatively higher surface area and acidity than SO_3H-Glc, and SO_3H-Xyl as well as all HTC catalysts. Furthermore, NH_3-TPD of solid acid catalysts indicated the main peak at low temperature (below 300 °C), which corresponds to weak acid sites of Brønsted acid sites. These physical characterizations showed that the BET surface area and the amounts and density of acid sites of the catalysts as determined by TPD were correlated to the catalytic activity of the solid catalyst. SO_3H-Suc was found to contain the highest surface area and the highest acid sites. The results, therefore, revealed the high catalytic performance of sulfonated carbon-based catalyst, particularly SO_3H-Suc, on the hydrolysis of eucalyptus. It should be noted that the morpho-

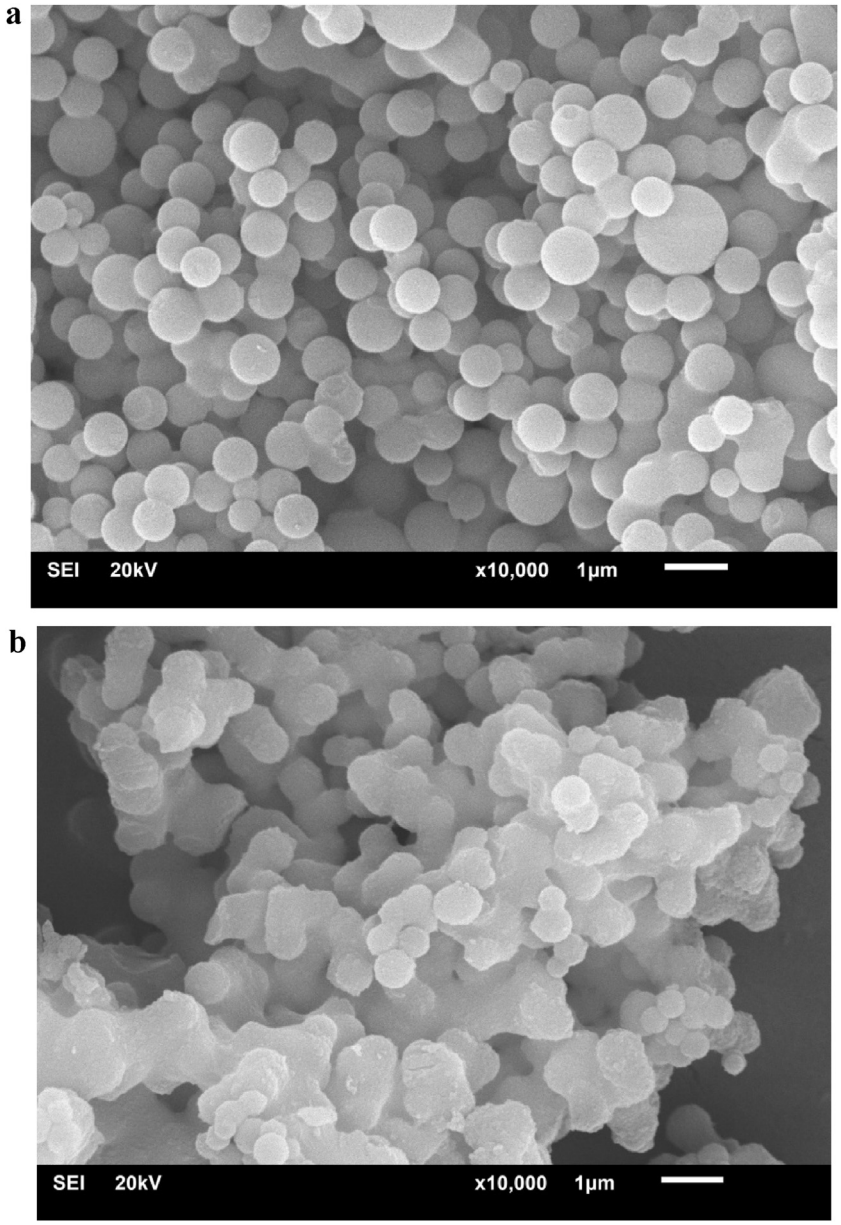

Fig. 2 – SEM images of (a) HTC prepared from sucrose; (b) SO_3H-Suc.

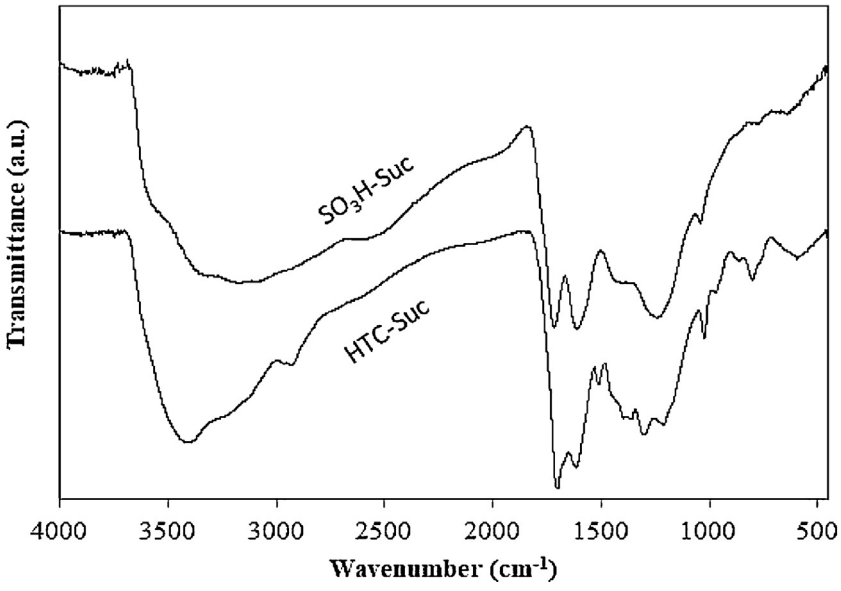

Fig. 3 – FTIR spectra of HTC prepared from sucrose and SO_3H-Suc.

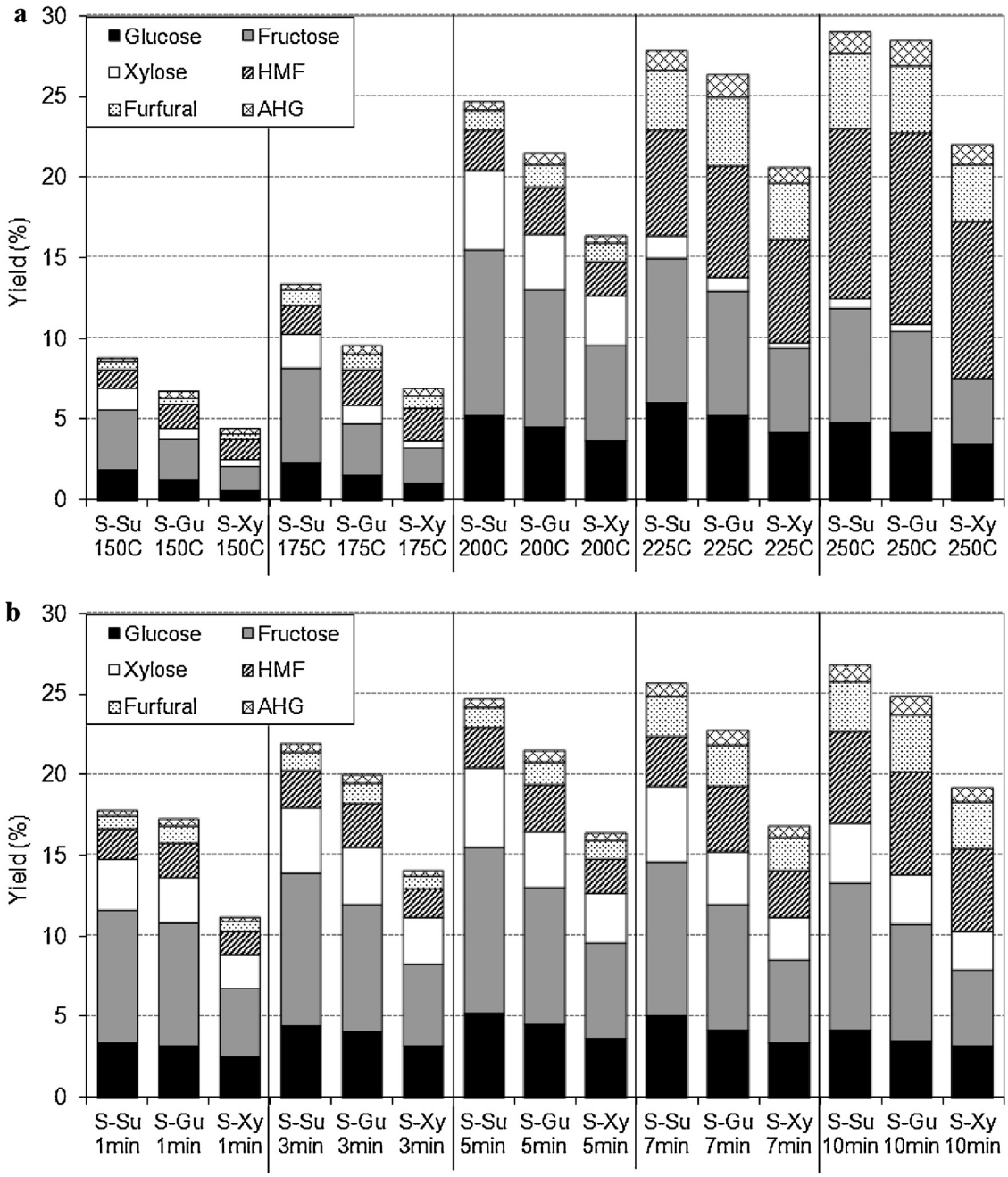

Fig. 4 – Effects of reaction parameters on the yield of liquid products from hydrolysis of milled eucalyptus. Reactions (6 mL) contained 1 biomass with 5% catalysts and were heated at varying temperatures for 5 min (a) and at 200 °C for varying times (b) S-Su: SO_3H-Suc; S-Gu: SO_3H-Glc; S-Xy: SO_3H-Xyl.

logical structures of SO_3H-Suc and HTC are shown in Fig. 2, which suggested that HTC particles are of spherical shape with smooth surfaces. SO_3H-Suc possesses rougher surfaces than HTC, which could be due to the surface coverage with sulfuric acid. The FTIR spectrums in Fig. 3 clearly indicated the presence of SO_3H group in SO_3H-Suc, confirmed by the stretching vibration bands of O=S=O and $-SO_3^{2-}$ at 1167 and 1027 cm^{-1}, respectively.

3.2. *Effects of hydrolysis conditions*

The effects of reaction temperature on the hydrolysis of eucalyptus in the presence of SO_3H-Suc, SO_3H-Glc, and SO_3H-Xyl were studied at varying temperature (150–250 °C) while keeping the reaction time constant at 5 min As shown in Fig. 4a, the reaction temperature was found to have a significant effect on the feedstock conversion and the yield of liquid products. The yield of C_6 sugars (i.e. glucose and fructose) increased with increasing reaction temperature from 150 °C to 225 °C and slightly dropped down at 250 °C while the yield of C_5 sugar (xylose) increased with increasing the reaction temperature up to 200 °C and considerably decreased at higher temperatures. On the other hand, marked increases of furfural, HMF, and AHG were detected at the temperature above 200 °C. The effects of reaction time were studied at a fixed reaction temperature of 200 °C (Fig. 4b). The yield of sugars increased steadily with increasing reaction time until 5 min and decreased at longer reaction time, which was opposite to the increasing formation of the sugar dehydration by-products with increasing time.

Based on the results, the overall rate of hydrolysis reaction for eucalyptus was faster than dehydration reaction at

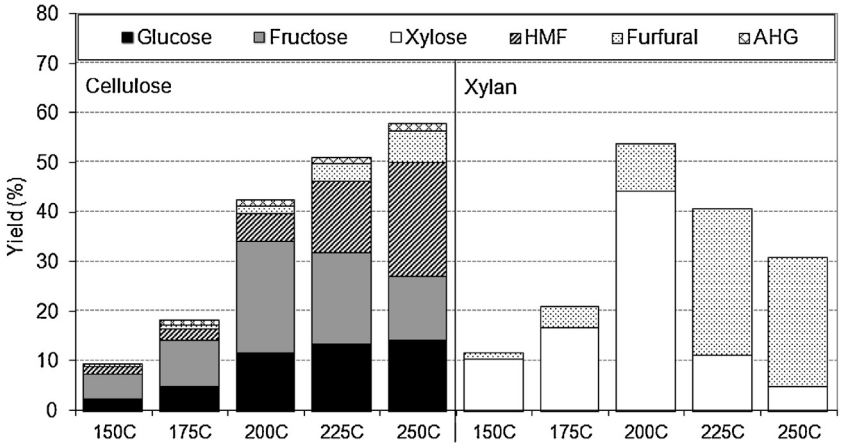

Fig. 5 – Effects of reaction temperature on the yield of liquid products from hydrolysis of cellulose (a) and xylan (b). Reactions (6 mL) contained 1 g milled eucalyptus and were heated at 200 °C for 5 min with 5% SO_3H-Suc catalyst.

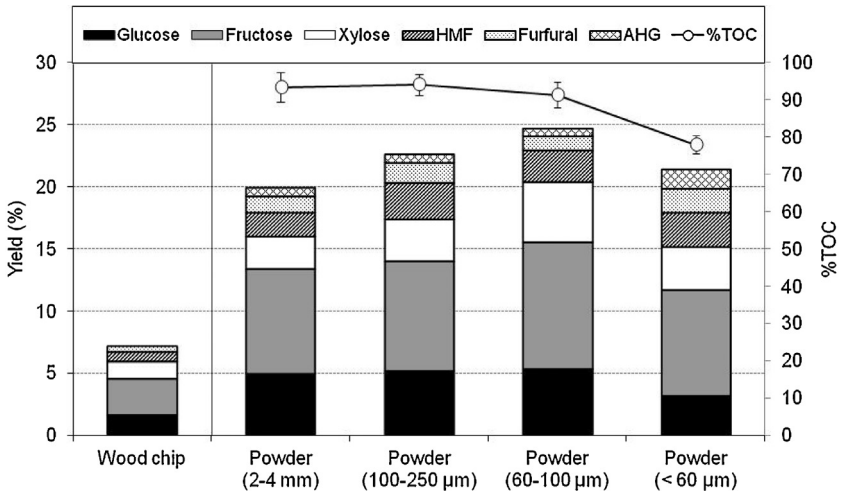

Fig. 6 – Effects of eucalyptus particle size on the yield of liquid products and TOC value from hydrolysis of eucalyptus. Reactions (6 mL) contained 1 g eucalyptus biomass with varying size ranges and were heated at 200 °C for 5 min with 5% SO_3H-Suc catalyst.

the temperature between 150–200 °C with the reaction time of 5 min while a higher rate of monosaccharide decomposition via dehydration was observed at the temperature above 200 °C, leading to the decreasing sugar production at high temperatures. This was correlated to the optimal temperature for hydrolysis of the cellulose and xylan. The highest C_6 and C_5 sugar yields were obtained at 200 °C from the hydrolysis of cellulose and xylan using SO_3H-Suc (Fig. 5), which is in good agreement with its physical and chemical properties as presented in Table 1. Glucose and fructose were the main products from the cellulose conversion at 200 °C or below while increasing amount of side-products particularly HMF was formed at higher temperatures. In term of product yield and selectivity, the temperature of 200 °C was determined as the optimum condition for cellulose conversion, at which the hydrolysis and isomerization reactions were maximized while the dehydration reaction was minimized. Xylose was the main product from hydrolysis of hemicellulose at 200 °C or below 200 °C while increasing furfural was formed at higher temperature from dehydration of xylose. Based on the results, the optimized conditions for the hydrolysis of eucalyptus in the presence of SO_3H-Suc was at 200 °C for 5 min, from which the highest total sugar yield (i.e. glucose, fructose and xylose) with relatively low selectivity toward undesired products (i.e. furan and AHG) can be obtained.

3.3. *Hydrolysis of pretreated eucalyptus under HCW in the presence of SO_3H-Suc*

Effects of physical processing and chemical pretreatment of eucalyptus were studied under the optimal hydrolysis conditions. In order to study the influence of biomass size on hydrolysis, the eucalyptus chips were milled and seived to varying size ranges. Reduction in particle size down to 60 μm led to enhanced hydrolysis efficiency from which the highest total sugar yield of 20.4% was obtained (Fig. 6). This could be due to the improvement of mass transfer limitation in the reaction. Further reduction in particle sizes resulted in decrease in sugar yield. This was in accoradance to analysis of total organic carbon which showed the TOC higher than >90% for the biomass with the size higher than 60 μm, indicating that the quantity of gaseous products from the reactions. However, the TOC value from the reaction with very fine particle sizes of eucalyptus (<60 μm) was only 78%, which suggested the conversion of biomass to gaseous by-products via the thermal cracking reaction. Hence, eucalyptus with the average particle size between 60–100 μm was then chosen for the pretreatment study.

Pretreatment of eucalyptus by alkali and alkaline peroxide led to increasing sugar yields from the hydrolysis reactions. Hydrolysis of eucalyptus was studied under the optimal

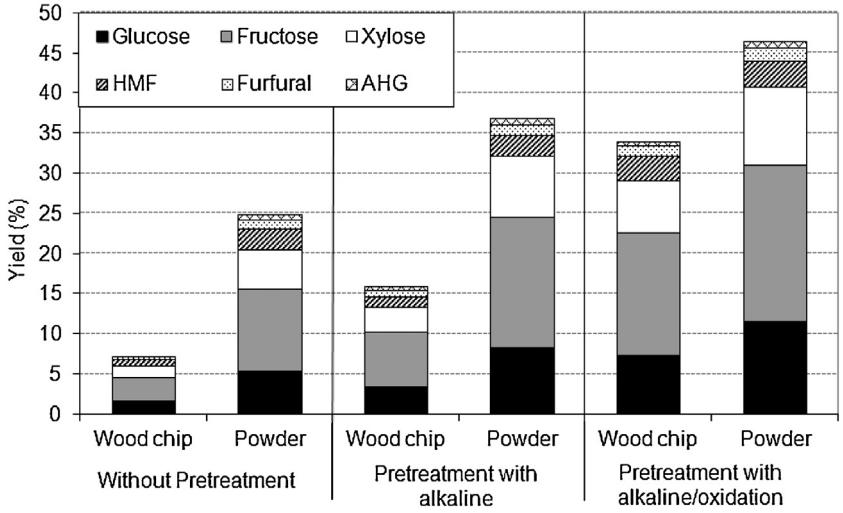

Fig. 7 – Effects of physical and chemical pretreatment on the yield of liquid products from hydrolysis of eucalyptus. Reactions (6 mL) contained 1 g pretreated eucalyptus chips or powder (60–100 μm) and heated at 200 °C for 5 min with 5% SO_3H-Suc catalyst.

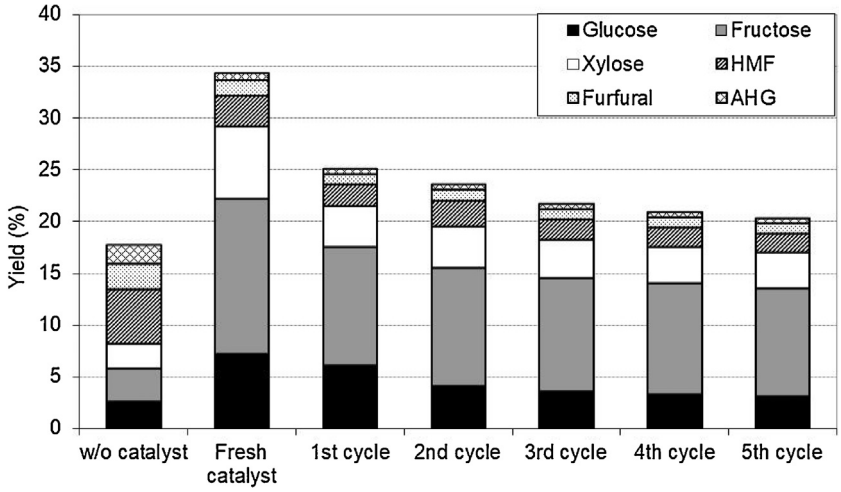

Fig. 8 – Reusability testing of SO_3H-Suc catalyst on hydrolysis of milled eucalyptus. Reactions (6 mL) contained 1 g biomass and heated at 200 °C for 5 min with 5% SO_3H-Suc catalyst.

reaction conditions. As shown in Fig. 7, the hydrolysis of pretreated eucalyptus exhibited significantly higher sugar yield and selectivity, particularly for the sample pretreated by alkaline oxidation process. The highest sugar yield of 40.7% was achieved from hydrolysis of the pretreated eucalyptus in powder form, whereas 28.9% yield of total sugars were produced from the reaction with pretreated wood chips compared to only 5.9% yield of total sugars obtained from the hydrolysis of non-pretreated eucalyptus wood chips. The result thus suggested the positive effects of chemical pretreatment prior to the catalytic hydrolysis process. Alkaline pretreatment was reported as an effective method for delignification of lignocellulosic biomass, while alkaline hydrogen peroxide using H_2O_2 under mild operational conditions was shown to promote partial lignin removal and solubization of hemicelluloses (Azzam, 1989). In this study, according to standard NREL analysis (Sluiter et al., 2008), 78.1% and 88.6% of lignin can be removed from the feedstock by alkali and alkaline peroxide pretreatments, respectively. This delignifification results in higher sugar yield production from the hydrolysis since it has been reported that, under HCW condition, lignin strongly inhibited the acid hydrolysis of cellulose and hemicellulose to glucose and xylose, respectively (Daorattanachai et al., 2013).

3.4. *Reusability of SO_3H-Suc*

The recycling of SO_3H-Suc on sequential batch hydrolysis of pretreated eucalyptus wood chips was studied under the optimized reaction conditions. After separating the catalyst from the reaction, the catalyst was washed and dried before re-testing under the same operating conditions. As shown in Fig. 8, a significant decrease in liquid product yield (27.1%) was observed after the first batch. Nevertheless, only slight reduction (8.0%) on the total liquid product yield was found from the 2nd to 5th fifth batches. This catalyst deactivation profile suggested the partial leashing of acid sites from the surface of solid acid catalysts under the experimental conditions. The results from NH_3-TPD techniques also confirmed the leaching of acids as shown by the decrease in total acid density to 12.2 μmol/m^2 after recycling for five batches. Therefore, to apply this SO_3H-Suc in the prolonged hydrolysis application, the catalyst regeneration by re-sulfonation is required. It should be noted that, in order to compare the degree of catalyst leaching, the leaching tests of SO_3H-Suc, SO_3H-Glc, and SO_3H-Xyl were performed by subjecting the catalysts in HCW condition (without the presence of eucalyptus) and measuring the acidity of post-reaction catalyst

Table 2 – Hydrolysis degradation of substrate (biomass and cellulose) to glucose with selected solid acid catalysts.

Catalyst	Type of substrates	Time [h]	Temp. [K]	Conversion [%]	Yield of glucose [%]
Sulfonated activated carbon (this study)	Pretreated eucalyptus	24	423	43	40.7
Amorphous carbon bearing from cellulose SO_3H, COOH and OH ($CH_{0.62}O_{0.54}S_{0.05}$)	Cellulose (microcrystalline)	3	373	Up to 100	4[a]
Silica/carbon nanocomposites	Cellulose (ball-milled)	24	423	61	50
Layered $HNbMoO_6$	Cellulose (microcrystalline)	12	403	n.r.[b]	1
Ru/CMK-3	Cellulose (ball-milled)	0.25	503	68	34

[modified from Van de Vyver et al., 2011].

[a] The main product in this reaction was water-soluble β-1,4-glucan (64% yield).
[b] n.r. = not reported.

as well as pH of water. It was found that the acidities of SO_3H-Glc, and SO_3H-Xyl decreased by 32.7% and 35.4% (compared to 24.3% observed over SO_3H-Suc). In addition, the pH of water after HCW in the presences of SO_3H-Glc, and SO_3H-Xyl reduced to 3.2 and 2.9, respectively, whereas that in the presence of SO_3H-Suc was 4.1. This result indicated that SO_3H-Suc showed the lowest leaching percentage and also confirmed that the reaction was mainly catalyzed by heterogeneous solid acid rather than homogeneous acid leached from the catalyst.

Compared to conventional reactions using liquid acids, hydrolysis of lignocelluloses using solid acid catalysts has distinct advantages on recycling, separation, and environmental friendliness with potential on generating less inhibitory by-products from sugar degradation according to the results in our study. Typically, carbon-based sulfonated catalysts have been prepared by two-step process (Suganuma et al., 2008; Hara, 2010; Tamthiengtrong, 2011). Firstly, the incomplete carbonized material (i.e. D-glucose, sucrose, cellulose) was heated for 1–5 h at 350–400 °C under N_2 flow to obtain amorphous carbon. Next, the amorphous carbon from step one was ground to a powder which was then boiled in concentrated H_2SO_4 (>96%) at 150 °C under N_2 flow for 10–15 h in order to add SO_3H group on the surface of amorphous carbon. In this present work, a one-step process was applied instead, from which the direct sulfonation of sugars (xylose, glucose, sucrose) under N_2 flow at 230–250 °C was used. The one-step process reported in this study is simple and requires less energy. From the experiments, it was found that the best type of catalyst for hydrolysis is SO_3H-Suc. SO_3H-Suc prepared by two-step process was also prepared and tested under optimum condition for comparison. It was found that similar range of sugar yield (29.8%) was obtained (compared to 29.1% achieved from hydrolysis of the pretreated eucalyptus in the presence of SO_3H-Suc prepared by one-step process). Nevertheless, after recycling for five times, higher deactivation was observed over SO_3H-Suc prepared by two-step process (32.4%). This indicated the higher stability of catalyst prepared by one-step process.

The specific surface area, pore size and pore volume, the active site concentration and acidic type are typically key determinants on solid acid performance. Solid acid catalysts for cellulose hydrolysis should contain a large number of Brønsted acid sites with good affinity for the substrates and stability under high temperature conditions. In this work, solid acid catalysts were characterized to determine their surface area and acid properties (i.e. amount of acid site (μmol/g), and density of acid site (μmol/m^2)) to correlate their physical and chemical properties with their hydrolysis performance. It was found that the catalytic activity trend is in good agreement with the acid density of these catalysts, from which the catalyst with high acid site density like SO_3H-Suc can enhance the great reactivity toward the hydrolysis reaction.

Performance of the solid acid catalysts on hydrolysis of lignocellulose depends on the intrinsic properties of the catalysts themselves and physicochemical characteristics of the biomass. According to the results in this present study, the pretreatment step led to markedly enhanced conversion yield. Physical treatment by size reduction with ball milling showed a strong effect on increasing sugar yield. A substantial increase in conversion yield was also achieved by alkaline delignification which could be further enhanced in the presence of hydrogen peroxide which catalyzing removal of hemicellulose and lignin by oxidation. Tamthiengtrong (2011) has reported the good hydrolysis activities of sulphonated activated carbon (AC-H_2SO_4)/phosphonated activated carbon (AC-H_3PO_4)/nitrated activated carbon (AC-HNO_3)/and hydrochorated activated carbon (AC-HCl), from which the highest sugars yield could be enhanced by applying H_3PO_4-activated carbon as catalyst. These results are in good agreement with this study. It has been indicated that solid acid catalysts have several favorable characteristics to replace homogeneous acid catalysts (i.e. H_2SO_4, HCl, and H_3PO_4) for the hydrolysis reaction such as high activity, high selectivity, long catalyst life and ease in recovery and reuse. Van de Vyver et al. studied the solid acid catalytic conversion of cellulose and summarized the performance of several solid chemocatalysts for the cellulose into glucose reaction as shown in Table 2 which compared performance of selected acid catalysts previous to those developed in this present work. The potential of carbonaceous solid acid (CSA) catalysts compared to the expensive silica/carbon nanocomposite, reported as the most potent catalyst for cellulose hydrolysis, is clearly seen as they can provide good reactant accessibility to the acidic sites of SO_3H and PO_3H_2 groups. The mechanism on hydrolysis of lignocellulosic biomass with CSA catalysts is similar to that of homogeneous acids, from which protons in SO_3H and PO_3H_2 attack the β-1,4 glycosidic bonds in the solid crystalline cellulose. This is attributed to an increase in acidity of SO_3H and PO_3H_2 groups on the carbon material with a decrease in the amount of water.

4. Conclusion

Sulfonated solid carbonaceous acid catalysts showed great hydrolysis performance as reflected by its high catalytic efficiency and selectivity under HCW conditions. Compared to conventional liquid acid catalysts, the developed SO_3H-Suc can be recycled in consecutive batch process with lower loss of sugars via dehydration during the hydrolysis reaction and is less corrosive to the equipment, resulting in overall

improvement in the performance of the hydrolysis reaction. The catalytic hydrolysis process using the heterogenous acid catalyst provides a potent alternative for conversion of lignocellulosic biomass to sugars with low degradation by-products for further production of biorefinery products.

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Competing interests

The authors declare that they have no competing interests.

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Corresponding Author: Dr. Artiwan Shotipruk,

Corresponding Author's Institution: Chulalongkorn University

First Author: Tat Boonyakarn

Order of Authors: Tat Boonyakarn; Piyaporn Wataniyakul; Panatpong Boonnoun; Armando T Quitain; Tetsuya Kida; Mitsuru Sasaki; Navadol Laosiripojana; Bunjerd Jongsomjit; Artiwan Shotipruk

Abstract: This study presents a novel catalysis system using the combination of Brønsted hydrothermal carbon-based acid (HTCG-SO3H) and Lewis acid catalysts for synergistic one-pot conversion of cellulose to levulinic acid (LA). Chromium chloride (CrCl3), among a number of other Lewis acidic metal chlorides, was found to give the highest LA yields, and was therefore used in combination with the HTCG-SO3H, for cellulose conversion to LA. At a proper operating condition; 5 wt.% of HTCG-SO3H, 0.015 M of CrCl3, and 200oC for 5 min, the use of CrCl3 and HTCG-SO3H together could considerably and synergistically enhance the LA yield compared with that obtained by CrCl3 alone (40 wt.% vs. 30 wt.%).

Suggested Reviewers: Youn-Woo Lee
Seoul National University
ywlee@snu.ac.kr
He is exploring the use of solvents for chemical and physical process. The current areas of application for such process are numerous and include material synthesis, chemical reactions, and separations. He has over 180 publications and 30 patents.

Jorge Beltramini
The University of Queensland
jorgeb@uq.edu.au
He is a senior research fellow with more than 25 years of experience in the main areas of solid state catalysis, material science, and petroleum refining technologies.

Joseph Auresenia
De La Salle University
joseph.auresenia@dlsu.edu.ph
He is expert in the main areas of heterogeneous catalyst as well as biotechnology and bioenergy.

March 6, 2018

Dear Editor,

Enclosed is an article entitled **"Enhanced Levulinic Acid Production from Cellulose by Combined Brønsted Hydrothermal Carbon and Lewis Acid Catalysts"**, authored by Tat Boonyakarn, Piyaporn Wataniyakul, Panatpong Boonnoun, Armando T. Quitain, Tetsuya Kida, Mitsuru Sasaki, Navadol Laosiripojana, Bunjerd Jongsomjit, and myself, submitted for consideration for publication in **Catalysis Communications**. In this article, a catalytic system of combing a Lewis acid and a new class of Brønsted acid catalyst, prepared by hydrothermal carbonization of glucose, followed by acid functionalization, was shown to synergistically enhance the production of levulinic acid from cellulose.

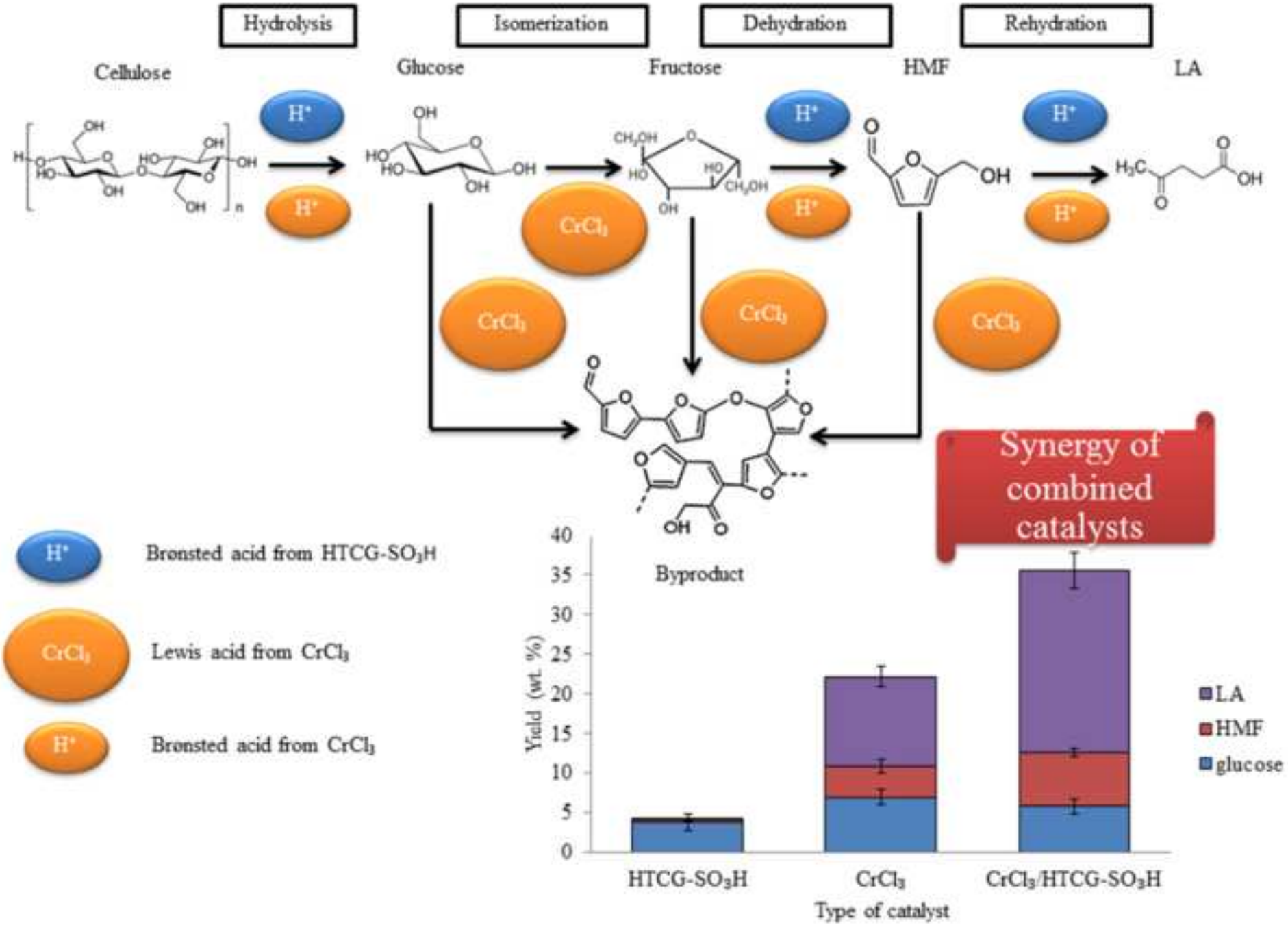
The article is original work and has been written by the stated authors who are all aware of its content and have approved its submission. The article has neither been published previously, nor it has been under consideration for publication elsewhere. The authors also confirm that no conflict of interest exists. In addition, if accepted, the article will not be published elsewhere in the same form or in any other languages, without the written consent of the publisher.

Should you have further questions regarding this paper, please contact me.

Sincerely,

Artiwan Shotipruk
Faculty of Engineering
Department of Chemical Engineering
Chulalognkorn University
Bangkok 10330, Thailand
Tel: (662) 218-6868
Fax: (662) 218-6877
E-mail: artiwan.sh@chula.ac.th

Graphical Abstract



Highlights

Enhanced Levulinic Acid Production from Cellulose by Combined Brønsted Hydrothermal Carbon and Lewis Acid Catalysts

- Among Lewis acidic metal chlorides, $CrCl_3$ gave the highest LA yield.
- $CrCl_3$ catalyst alone promoted glucose isomerization with drawback of side reactions.
- HTCG-SO_3H promoted hydrolysis, dehydration, and rehydration.
- Combination of $CrCl_3$ with HTCG-SO_3H gave higher LA yield than using $CrCl_3$ alone.
- 5 wt.% HTCG-SO_3H, 0.015 M $CrCl_3$, at 200°C for 5 min was a suitable condition.

Enhanced Levulinic Acid Production from Cellulose by Combined Brønsted Hydrothermal Carbon and Lewis Acid Catalysts

Tat Boonyakarn[a], Piyaporn Wataniyakul[a], Panatpong Boonnoun[b], Armando T. Quitain[c], Tetsuya Kida[c], Mitsuru Sasaki[c], Navadol Laosiripojana[d], Bunjerd Jongsomjit[a], Artiwan Shotipruk[a]*

[a]Chemical Engineering Research Unit for Value Adding of Bioresources, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Phayathai Road, Bangkok 10330, Thailand

[b]Department of Industrial Engineering, Faculty of Engineering, Naresuan University, Phitsanulok 65000, Thailand

[c]Department of Applied Chemistry and Biochemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860-8555, Japan

[d]The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Prachauthit Road, Bangmod, Bangkok 10140, Thailand

* Corresponding author. Tel: +66-2-218-6868; Fax: +66-2-218-6877

Email: Artiwan.Sh@chula.ac.th (A. Shotipruk)

Abstract

This study presents a novel catalysis system using the combination of Brønsted hydrothermal carbon-based acid (HTCG-SO_3H) and Lewis acid catalysts for synergistic one-pot conversion of cellulose to levulinic acid (LA). Chromium chloride ($CrCl_3$), among a number of other Lewis acidic metal chlorides, was found to give the highest LA yields, and was therefore used in combination with the HTCG-SO_3H, for cellulose conversion to LA. At a proper operating condition; 5 wt.% of HTCG-SO_3H, 0.015 M of $CrCl_3$, and 200^oC for 5 min, the use of $CrCl_3$ and HTCG-SO_3H together could considerably and synergistically enhance the LA yield compared with that obtained by $CrCl_3$ alone (40 wt.% vs. 30 wt.%).

Keywords: Cellulose; Levulinic acid; hydrothermal carbon-based acid catalyst; Lewis acid; Brønsted acid

1. Introduction

Lignocellulosic biomass consisting mainly of cellulose, hemicellulose and lignin, is recently considered as a promising renewable material for the production of high valuable chemicals such as hydroxymethylfurfural (HMF) and levulinic acid (LA). LA especially, has gained increasing interest as an alternative to petroleum-based chemicals, for uses as, plasticizer, coating, fuel additive and antifreeze, and in processing of resin, textile, and animal feed [1].

For LA production from biomass, cellulose in biomass is generally decomposed through hydrolysis reaction to simple sugar such as glucose, which is then converted to HMF by dehydration. Subsequently, HMF is rehydrated to LA. In general, Brønsted acid catalysts are used for the hydrolysis of cellulose, dehydration of sugars and rehydration of HMF. However, using Brønsted acid catalyst alone such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl), carbon-based acid [2], graphene oxide (GO) [3, 4] and so forth, is inefficient for this particular cascaded reaction. This is due to the difficulty of dehydration of glucose directly to HMF. As a result, an additional isomerization reaction is generally needed to first convert glucose to fructose, which is more easily dehydrated. The isomerization reaction, however, requires use of a Lewis acid [5-9] or a Brønsted base [10].

Recently, improvement of HMF and LA yields from biomass has been accomplished by bi-functional catalysts [11-20], by which catalysts with two functional groups, one being the Brønsted acid, and another being enzyme, Lewis acid, or Brønsted base are applied. Interestingly, Lewis acidic metal salts; the intrinsic bi-functional catalyst such as salts of Cr(III), Cr(II), Al(III), Zn(II), Sn(IV), Fe(III), Cu(II) for example, have been reported to sufficiently drive hydrolysis, dehydration, and rehydration reactions without external addition of Brønsted acid. However, all acidic metal salts give poor selectivity to HMF and LA, since

Lewis site of acidic metal salts generally simultaneously promote the formation of humin byproduct, especially from sugars and HMF [21].

To increase the selectivity of HMF and LA, the addition of external Brønsted acid to Lewis acidic metal salts is recommended [21]. The synergistic effect of combined homogenous Lewis acid and external Brønsted acids have been confirmed for biomass conversion in a number of previous research studies. These include the use of chromium chloride ($CrCl_3$) and HCl [22], $CrCl_3$ and ammonium halides [23], $CrCl_3$ and carbon dioxide [24], aluminum chloride ($AlCl_3$) and HCl [25], aluminum trifluoromethanesulfonate ($Al(CF_3SO_3)_3$) and oxalic acid ($H_2C_2O_4$) [26]. Despite the improvement in the yields of HMF and LA by the combined homogenous Brønsted acid and Lewis acid systems, the homogeneous external Brønsted acids are highly corrosive, and are thus not environmentally friendly. As an alternative, a heterogeneous Brønsted acid catalyst is of considerable interest, particularly those prepared from low cost carbon materials such as biomass, sugar and so forth. Preparation of the carbon-based acid catalyst generally requires two main steps: carbonization, which is normally carried out by incomplete combustion, followed by functionalization of the resulted carbonized material by acid (normally sulfuric acid) [27, 28]. Recently, hydrothermal carbonization is gaining considerable attention as a process for the preparation of carbon material used as a catalyst support. Since the process is carried out in hot water at relatively mild temperatures under auto-generated pressure, prior raw material drying step can be omitted, and thus lowering the energy consumption, compared to the incomplete combustion process [29-31].

In this work, the combination of Lewis acidic metal salt and hydrothermal carbon-based acid catalyst (HTCG-SO_3H) for cellulose conversion to obtain LA is therefore investigated. The most suitable metal salt was firstly selected based on cellulose conversion. The combination of the metal salt and HTCG-SO_3H was then studied in detail, particularly to

determine the effects of HTCG-SO_3H addition, reaction temperature, reaction time, HTCG-SO_3H dosage and the concentration of metal salt on cellulose conversion.

2. Materials and Methods

2.1 Materials and chemicals

Glucose, hydroxymethylfurfural (HMF), levulinic acid (LA), concentrated sulfuric acid (98%), acetone, ethanol, methanol and chromium (III) chloride (hexahydrate) ($CrCl_3$), manganese (II) chloride ($MnCl_2$), cadmium chloride ($CdCl_2$), cobalt (II) chloride ($CoCl_2$), iron (III) chloride (hydrate) ($FeCl_3$) and iron (II) chloride (tetrahydrate) ($FeCl_2$) were purchased from Wako Pure Chemical Company (Osaka, Japan). Cellulose powdered was purchased from HiMedia Laboratories Pvt. Ltd. (Mumbai, India).

2.2 Synthesis of hydrothermal carbon-based acid catalyst from glucose

To prepare HTCG-SO_3H, a two-step process consisting of hydrothermal carbonization and acid functionalization was prepared following the procedure of Wataniyakul et al. (2018). For hydrothermal carbonization, 30 g of glucose and 300 ml of deionized water were mixed in a 520 ml SUS-316 stainless-steel closed batch reactor and the reactor was then heated at 220°C for 6 hours. After the reaction was completed, the resulting black solid sample or hydrothermal carbon (HTCG) was washed with water, ethanol, and acetone, each for 1 hour under sonication. The resulting HTCG was filtered by whatman filter paper (No.1) and dried at 110°C overnight in a hot air oven. For the acid functionalization, 50 ml of concentrated sulfuric acid was added to 5 grams of dried HTCG. The mixture, in a 3-neck rounded bottom flask was then heated at 150°C for 15 hours. After the heating process was complete, the resulting solid was washed with boiling distilled water until no pH change in the wash water was observed. The solid catalyst (HTCG-SO_3H) was then washed with 500 ml of ethanol,

then with 300 ml of acetone, dried overnight at 110 °C, and was then ground to powder. The detailed physicochemical characterization results of the HTCG and HTCG-SO_3H prepared by the aforementioned procedures were reported in our previous work [32].

2.3 Cellulose conversion tests

In this study, a number of cellulose conversion tests were carried out. Firstly, six commonly used metal salts: $FeCl_2$, $FeCl_3$, $CoCl_2$, $MnCl_2$, $CdCl_2$ and $CrCl_3$ were compared, and the most suitable metal salt was selected based on the catalytic activity on cellulose conversion. Secondly, the use of Brønsted HTCG-SO_3H in combination with the selected Lewis acid catalysts was evaluated on cellulose conversion. The results were compared with those obtained from the reactions catalyzed by a single catalyst (either HTCG-SO_3H or the Lewis acid catalyst). In addition, the effects of various process variables were determined in the reaction system of combined catalysts. In all cases, the cellulose conversion reactions were carried out in an 8.8 ml SUS-316 stainless-steel closed batch reactor (AKICO Co., Japan). In the first set of experiment to determine the most suitable Lewis acid catalyst, 0.1 g of cellulose and 5 ml of a 0.005 M solution of metal salt (in DI water) were charged into the reactor. The reactor was then shaken and heated to 200°C by an electric heater, connected to a temperature controller. The reaction was then allowed to take place for 5 min, after which the reactor was quenched in a water bath. With an additional amount of 5 ml of de-ionized water, the liquid reaction product and the remaining solid were completely removed from the reactor, and were separated from each other by a Whatman filter paper (No. 1). The amounts of glucose, HMF and LA in the liquid products were determined by a high performance liquid chromatography (HPLC).

The most suitable Lewis acid, yielding the highest LA yield, was then combined with HTCG-SO_3H and the combined catalysts were evaluated for cellulose conversion. As a

preliminary evaluation of the combined catalyst, 0.1 g of cellulose and 5 ml of the selected metal salt solution (in DI water) were used and the reaction was carried out at 200°C for 5 min. Furthermore, detailed cellulose conversion experiments were also carried out to determine the effect of reaction temperature (160-220°C), reaction time (0-60 min), HTCG-SO_3H dosage (0-40 wt. %) and metal salt concentration (0-0.02 M) on the glucose, HMF and LA yields.

The quantification of glucose, HMF, and LA in the liquid reaction product was conducted using a HPLC (JASCO AS-2055 plus, Japan) consisting of a Jasco RI-2031 plus detector, Jasco UV-970 detector, Jasco PU980 pump system, sugai U-620 column heater and a Jasco AS-2055 plus automated sampler injector equipped with a Shodex SUGAR SH1011 (8.0mmID*300 mm) column at 60°C. The concentrations of HMF and LA were analyzed based on UV absorbance at 220 nm and the concentrations of glucose were analyzed based on RI. Perchloric acid ($HClO_4$) was used as the eluent at a flow rate of 0.5 ml/min. The sample injection volume was 10 µl. The retention time for glucose, HMF and LA were 16.0, 39.4, and 23.3 min, respectively. The yields of the reaction products: glucose, HMF and LA were calculated as mass percentages of the products to the mass of the starting cellulose.

3. Results and Discussion

3.1 Selection of metal salt as Lewis acid catalyst

Based on the evaluation of six different metal salts, whose results are shown in **Fig. 1,** it was observed that various types of metal salt resulted in different yields of HMF and LA under identical conditions, and in the decreasing order: $CrCl_3$> $FeCl_2$= $FeCl_3$> $CoCl_2$ > $MnCl_2$> $CdCl_2$. When $CoCl_2$, $CdCl_2$, and $MnCl_2$ were used as catalysts, low glucose, HMF and LA yields were obtained. The reason for these findings has been clarified in a previous study [33], in which the importance of the acidity of metal chloride as well as the type of

metal were described to be key attributes to cellulose conversion. Low acidity metal chlorides such as $CoCl_2$, $CdCl_2$ and $MnCl_2$ (~pH 7) lack catalytic activity for cellulose conversion to glucose, and as a result, HMF and LA yields were low. It is also interesting to note that when Fe type catalysts were used, the yields of HMF and LA were relatively low, while that of glucose was relatively high. Having high acidity, $FeCl_3$ (~pH 2.5) was expected to have high catalytic activity for cellulose hydrolysis, however, the Fe type metal chlorides are not favorable for glucose isomerization compared with Cr type. $CrCl_3$ (~pH 3.8) which is relatively favorable in term of acidity, and is highly favorable in term of metal type, was found to give the highest overall yields of cellulose conversion products (glucose, HMF and LA). It was therefore selected for use in combination with HTCG-SO_3H in the subsequent study.

3.2 Combination of Lewis acid catalyst with hydrothermal carbon-based acid catalyst

Fig. 2 shows the comparison of glucose, HMF and LA yields from cellulose conversion carried out at 200^{o}C for 5 min, catalyzed by three systems of catalysts: HTCG-SO_3H, $CrCl_3$, and the two catalysts combined. As HTCG-SO_3H is a carbon-based Brønsted acid catalyst, it is expected to catalyze cellulose hydrolysis, but is inefficient for further conversion of glucose to HMF [2], the LA yield of the reaction catalyzed by HTCG-SO_3H alone was therefore expected to be low (**Fig. 2**). On the contrary, significantly higher LA yield was observed using $CrCl_3$ alone. This is due to the presence of ion complex, $[Cr(H_2O)_5OH]^{2+}$, formed in presence of water, that catalyzes isomerization of glucose to fructose, and the presence of the intrinsic Brønsted acidity, that drives hydrolysis, fructose dehydration to HMF, and further HMF rehydration to LA. Nevertheless, Lewis acid sites are non-selective, as they catalyze not only the aldose-to-ketose isomerization, but also the side reactions such as the generation of humin, an undesirable product, from sugars as well as

from HMF [21]. By working synergistically with the $CrCl_3$ catalyst, the addition of HTCG-SO_3H as a Brønsted acid catalyst led to approximately two folds enhancement of LA yield (from 11.2 wt. % to 22.9 wt. %). In agreement with previous studies, the result here demonstrated that further improvements in LA yield could be achieved by addition of a Brønsted acid catalyst, to facilitate the hydrolysis of cellulose, dehydration of fructose, and rehydration of HMF to LA before the side reactions took place by the action of the Lewis acid [21]. Given these results, further studies were conducted at various conditions to better gain the insight on the combined effect of $CrCl_3$ and HTCG-SO_3H catalysts, and to find the most suitable reaction conditions.

3.3 Effects of temperature and time

The glucose, HMF and LA yields obtained from cellulose conversion carried out under different reaction temperatures and times are shown in **Fig. 3**. As seen from **Fig. 3**, at the reaction temperatures of 160^{o}C and 180^{o}C, the yields of all products were relatively low at all reaction times. As the reaction temperatures increased to 200^{o}C and 220^{o}C, the increase in the overall yields of all products was observed due to the increased rates of reaction at higher temperatures. In addition, at high temperatures, the number of $[Cr(H_2O)_5OH]_2^+$ complexes and the H^+ ions increased; with the former, promoting glucose isomerization, while the latter, promoting hydrolysis, dehydration, and rehydration [22].

The results in **Fig. 3** also clearly demonstrated the influence of reaction time on cellulose conversion. At the reaction temperatures between 160^{o}C and 200^{o}C, glucose and HMF yields increased initially with time, and started to decrease after a certain point. While LA, on the other hand, continued to increase with time, suggesting that glucose was readily converted to HMF, and HMF to LA as the reaction proceeded. This was also true for the reaction at 220°C, with the glucose and HMF yields decreased abruptly from 0 to 5 min. At

220°C, the maximum LA yield was observed at the reaction time of 20 min to be 37 wt.%. It is, nevertheless, interesting to note that, at this temperature, LA yield dropped considerably from 37 wt.% to 19.5 wt.% upon increasing the reaction time from 20 min to 40 min. This result suggested that the LA was decomposed at high temperature and long time, which is in agreement with the study of Yan et al., 2008 which reported that LA was easily dehydrated to unsaturated lactone above approximately 200°C. Because of the observed instability of LA at 220°C, the reaction temperature and time were fixed at 200°C and 5 min in the subsequent study, in which the effects of HTCG-SO_3H catalyst dosage and $CrCl_3$ concentration on the production of LA were further determined. At 200°C and 5 min, not only does LA remain relatively stable, the yield of HMF, which is the LA precursor, were found to be at maximum, which would potentially provide rooms for the improvement of LA production.

3.4 Effect of hydrothermal carbon-based acid catalyst dosage

For cellulose conversion carried out at 200°C for 5 min, the results in **Fig. 4** clearly demonstrated the considerable influence of the catalyst dosage on cellulose conversion. Specifically, the increase in HTCG-SO_3H dosage from 0 to 5 wt.% resulted in significant increase in HMF and LA yields. The highest LA yield of 22.9 wt.% was observed at 5 wt.% HTCG-SO_3H dosage. At higher HTCG-SO_3H dosage from 10 wt.% to 40 wt.%, overall LA yield decreased with increasing HTCG-SO_3H dosage, whereas the overall glucose yield, on the other hand, increased. This could be due to the fact that the external Brønsted acid added to the system drove the $CrCl_3$ hydrolysis backward, causing the shift of active form of chromium chloride (for glucose isomerization), $[Cr(H_2O)_5]OH^{2+}$ to the less active form, $Cr(H_2O)_6^{3+}$ [22]. This result, therefore, suggested that the excess amount of HTCG-SO_3H inhibited glucose isomerization, and was likely to have a negative impact on LA production.

3.5 Effect of $CrCl_3$ concentration

Unlike increasing HTCG-SO_3H, increasing $CrCl_3$ concentration favored cellulose conversion, especially in glucose isomerization. As seen in **Fig. 5**, at high concentration of $CrCl_3$ (from 0.005 M to 0.02 M), both glucose and HMF yields decreased, since glucose and HMF can be more readily converted to LA in presence of $[Cr(H_2O)_5]OH^{2+}$ ion complexes and H^+ ions, respectively. As seen LA yields in **Fig 5**, the LA yields obtained from the system of combined catalysts were higher than those of $CrCl_3$ alone, for the entire $CrCl_3$ concentration range studied. In both cases, the increased LA yields with increasing $CrCl_3$ concentrations were evident. These results confirmed the synergistic effect of the combination of $CrCl_3$ and HTCG-SO_3H. The presence of HTCG-SO_3H promoted not only hydrolysis, dehydration and rehydration, but also reduced side reactions caused by $CrCl_3$. Comparable LA yields (ca. 40 wt. %) were found at $CrCl_3$ concentrations of 0.02 and 0.015 M. It is noted the results in the current study and those in literature could not directly be compared, since different biomasses and different experimental conditions were employed. To the best of our knowledge, only one study reported the LA yield from the conversion of cellulose [24], using combined Brønsted acids (HCl, H_2SO_4, or CO_2) and $CrCl_3$ as Lewis acid catalysts (**Table 1**). The slightly higher LA yield obtained in the current study was possibly due to higher reaction temperature, despite the much shorter reaction time.

4. Conclusions

The synergistic effect of the combination of HTCG-SO_3H as Brønsted acid and $CrCl_3$ as Lewis acid on cellulose conversion to LA was demonstrated. Under a suitable condition of 5 wt.% of HTCG-SO_3H, 0.015 M of $CrCl_3$, 200^oC and 5 min, approximately 40 wt.% LA yield could be produced in a one-pot cellulose conversion. Our study was the first to show that heterogeneous Brønsted acid (HTCG-SO_3H), which can be produced from low cost

renewable carbon sources, is a highly effective catalyst for the production of valuable biomass derived chemicals, when used in combination with Lewis acid.

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Figure Captions

Fig. 1

Yields of glucose, HMF and LA from cellulose conversion at 200^{o}C for 5 min, catalyzed with various acidic metal salts (0.005 M).

Fig. 2

Yields of Glucose, HMF and LA from cellulose conversion at 200^{o}C for 5 min, catalyzed with $CrCl_3$ (0.005 M), HTCG-SO_3H (5 wt.%), and both catalysts combined.

Fig. 3

Effects of temperature and time on yields of glucose, HMF, and LA from cellulose conversion with combination of $CrCl_3$ (0.010 M) and HTCG-SO_3H (10 wt.%).

Fig. 4

Effects of HTCG-SO_3H dosage on yields of glucose, HMF and LA from cellulose conversion at 200^{o}C for 5 min, catalyzed with combined $CrCl_3$ (0.005 M) and HTCG-SO_3H catalysts.

Fig. 5.

Effects of $CrCl_3$ concentration on yields of glucose, HMF, and LA from cellulose conversion at 200^{o}C for 5 min, catalyzed with combined $CrCl_3$ and HTCG-SO_3H (5 wt.%) catalysts.

Table 1: Comparison of reaction conditions and LA yields for cellulose conversion catalyzed by various systems of combined Brønsted acid and Lewis acid catalysts.

Entry	Brønsted acid (concentration)	Lewis acid (concentration)	LA (wt.%)	time (min)	Temperature (^{o}C)	Reference
1	HCl (0.25 M)	$CrCl_3$ (0.017 M)	32	90	160	[24]
2	H_2SO_4 (0.25 M)	$CrCl_3$ (0.017 M)	23	90	160	[24]
3	CO_2 (4 MPa)	$CrCl_3$ (0.017 M)	19	90	160	[24]
4	CO_2 (4 MPa)	$CrCl_3$ (0.017 M)	22	90	180	[24]
5	HTCG-SO_3H (5 wt.%)	$CrCl_3$ (0.015 M)	40	5	200	This work

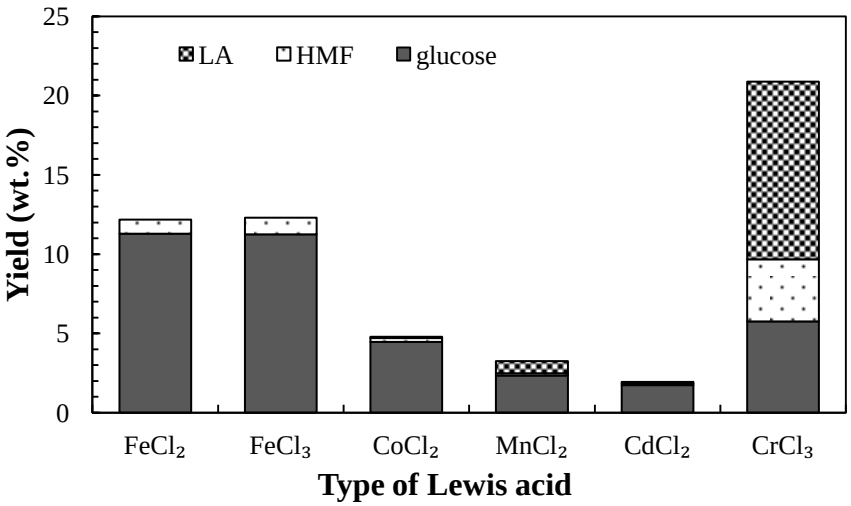

25
20
15
10
5
0
LA
HMF
glucose
Yield (wt.%)
FeCl2
FeCl3
CoCl2
MnCl2
CdCl2
CrCl3
Type of Lewis acid

Fig. 1

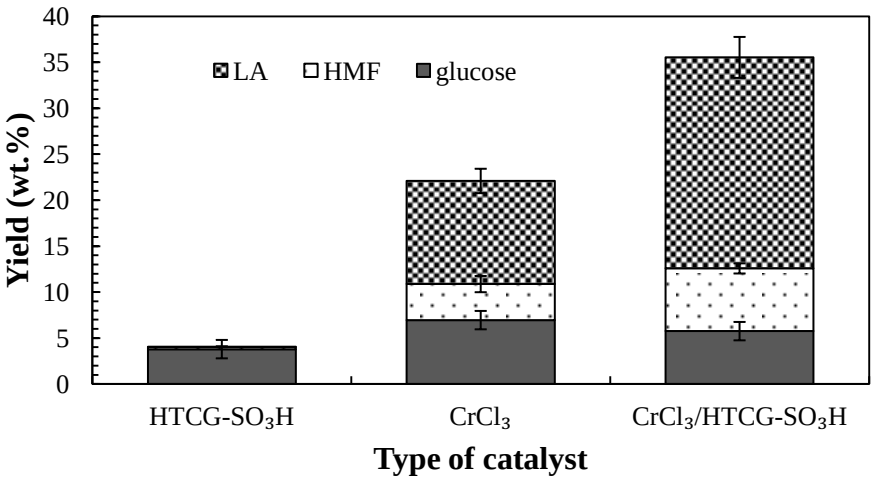
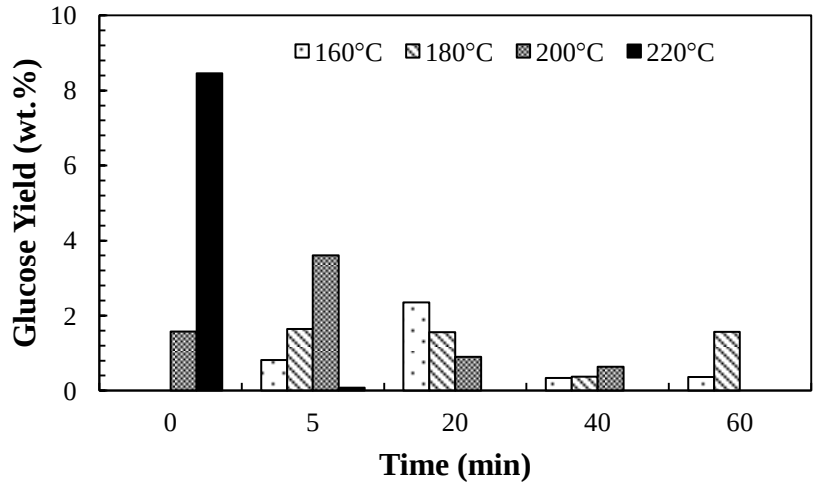
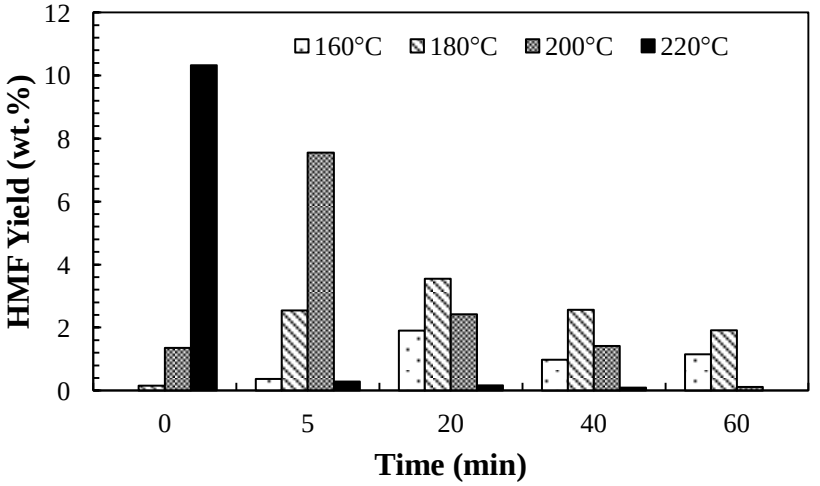

40
35
30
25
20
15
10
5
0
LA
HMF
glucose
Yield (wt.%)
HTCG-SO3H
CrCl3
CrCl3/HTCG-SO3H
Type of catalyst

Fig. 2


160°C
180°C
200°C
220°C
Glucose Yield (wt.%)
10
8
6
4
2
0
0
5
20
40
60
Time (min)


160°C
180°C
200°C
220°C
HMF Yield (wt.%)
12
10
8
6
4
2
0
0
5
20
40
60
Time (min)

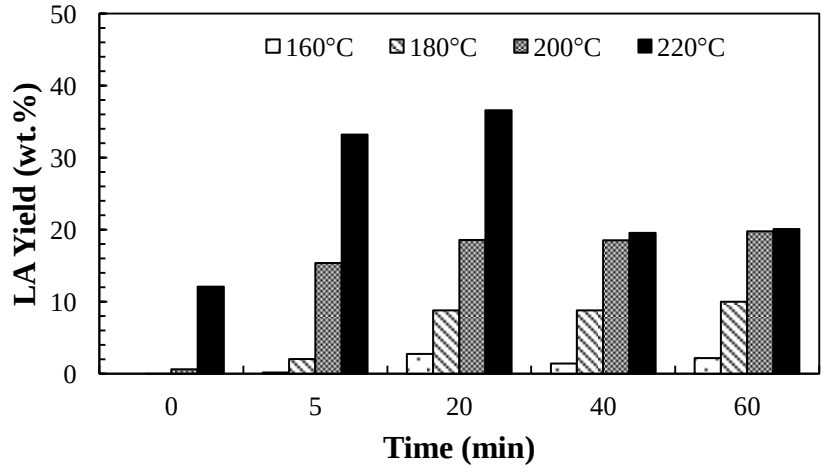

160°C
180°C
200°C
220°C
LA Yield (wt.%)
50
40
30
20
10
0
0
5
20
40
60
Time (min)

Fig. 3

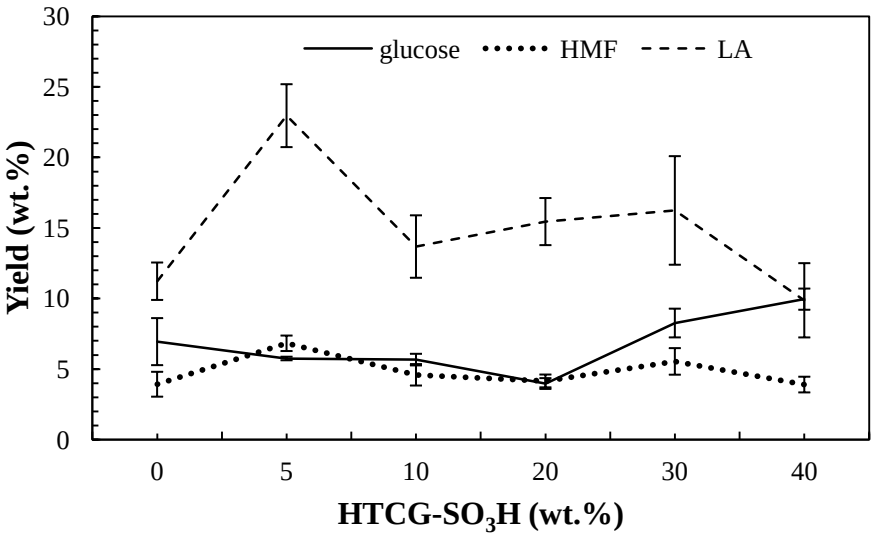
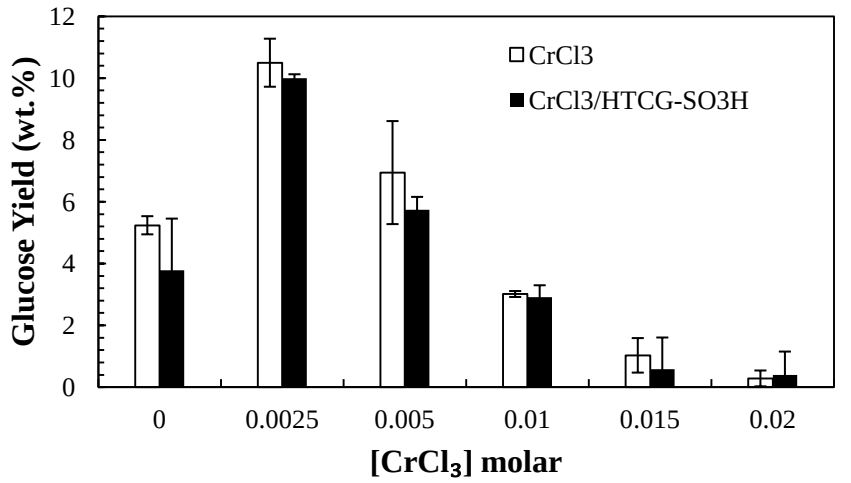
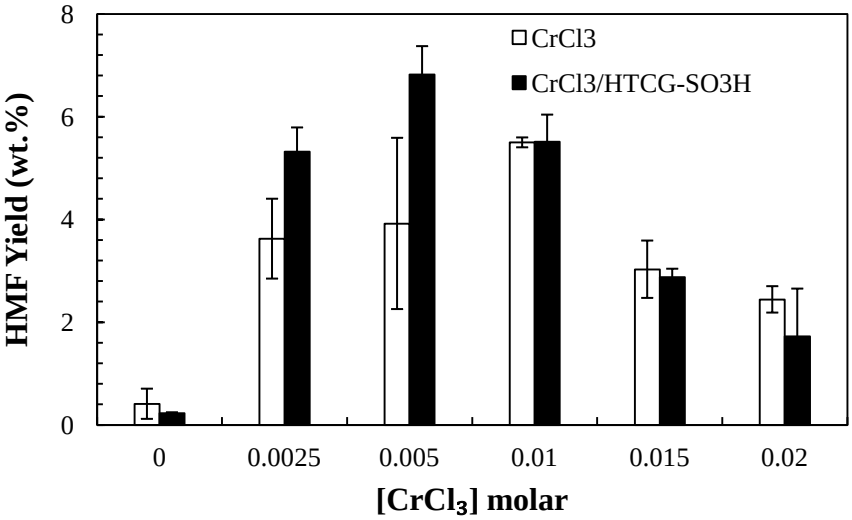

glucose
HMF
LA
Yield (wt.%)
HTCG-SO3H (wt.%)
0
5
10
15
20
25
30
0
5
10
20
30
40

Fig. 4


Glucose Yield (wt.%)
12
10
8
6
4
2
0
CrCl3
CrCl3/HTCG-SO3H
0
0.0025
0.005
0.01
0.015
0.02
[CrCl3] molar


HMF Yield (wt.%)
8
6
4
2
0
CrCl3
CrCl3/HTCG-SO3H
0
0.0025
0.005
0.01
0.015
0.02
[CrCl3] molar

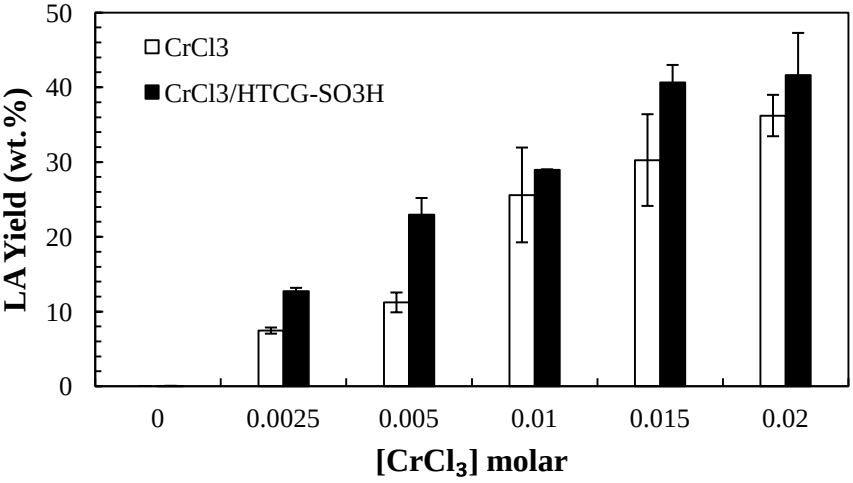

LA Yield (wt.%)
50
40
30
20
10
0
CrCl3
CrCl3/HTCG-SO3H
0
0.0025
0.005
0.01
0.015
0.02
[CrCl3] molar

Fig. 5