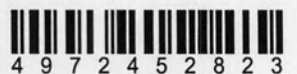


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CATALYTIC CRACKING OF WASTE FROM BIODIESEL PRODUCTION
USING Al-SBA-15


Mr. Rangsan Chakkasemkij

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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Chulalongkorn University
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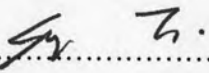
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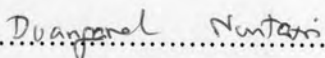
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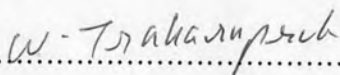
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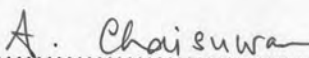

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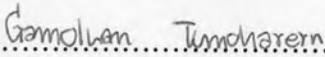
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สามารถสังเคราะห์เอสบีเอ-15 ซึ่งเป็นซิลิกาที่มีรูพรุนขนาดกลางทรงหกเหลี่ยมด้วยวิธีไฮโดรเทอร์มัลในตัวกลางที่เป็นกรด (พีเอชน้อยกว่า 1) ใช้เทรปล็อกโคพอลิเมอร์ชนิดพอลิเอทิลีนออกไซด์₂₀-พอลิโพรพิลีนออกไซด์₇₀-พอลิเอทิลีนออกไซด์₂₀ หรือ PEO₂₀PPO₇₀PEO₂₀; P123 เป็นสารขึ้นนำโครงสร้างมีองค์ประกอบของเจลเป็น 1.00 TEOS : 1.65 × 10⁻² P123 : 6.95 HCl : 140 H₂O ได้สังเคราะห์ตัวเร่งปฏิกิริยาอะลูมิเนียม-เอสบีเอ-15 ที่มีค่าอัตราส่วนโดยโมลของซิลิกอนต่ออะลูมิเนียมต่างๆ โดยการกวนเอสบีเอ-15 ในสารละลายโซเดียมอะลูมิเนต เป็นเวลา 12 ชั่วโมง แลกเปลี่ยนไอออนโซเดียมของอะลูมิเนียม-เอสบีเอ-15 ด้วยโปรตอน โดยการรีฟลักซ์ด้วยสารละลายแอมโมเนียมคลอไรด์ที่มีความเข้มข้น 0.01 โมลาร์ เป็นเวลา 24 ชั่วโมง จากนั้นตรวจสอบลักษณะเฉพาะของตัวเร่งปฏิกิริยาที่สังเคราะห์ได้ด้วยเทคนิคการเลี้ยวเบนของรังสีเอกซ์ เทคนิคการดูดซับไนโตรเจน การคายรังสีจากอะตอมโดยใช้พลาสมาเหนี่ยวนำ อะลูมิเนียมนิวเคลียร์แมกเนติกเรโซแนนซ์สำหรับสถานะของแข็ง และกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด ทดสอบความว่องไวของตัวเร่งปฏิกิริยาเอสบีเอ-15 ทั้งที่มีและไม่มีความเป็นกรดด้วยปฏิกิริยาการแตกตัวของเสียจากการผลิตไบโอดีเซลที่ความดันบรรยากาศ ภายใต้ภาวะที่แตกต่างกัน องค์ประกอบโดยประมาณของของเสียจากการผลิตไบโอดีเซลคือ กลีเซอรอล 37.18% เถ้า 6.49% น้ำ 1.85% และสารอินทรีย์อื่นที่ไม่ใช่กลีเซอรอล 54.48% ที่พีเอช 10.47 ด้วยความหนาแน่น 1.03 กรัมต่อมิลลิลิตร ภาวะที่เหมาะสมสำหรับการแตกตัวของของเสียจากการผลิตไบโอดีเซลคือที่อุณหภูมิ 400 องศาเซลเซียส ด้วย 10% โดยน้ำหนักของตัวเร่งปฏิกิริยาต่อของเสียจากการผลิตไบโอดีเซล เมื่อใช้อะลูมิเนียม-เอสบีเอ-15 เป็นตัวเร่งปฏิกิริยาค่าการเปลี่ยนของเสียจากการผลิตไบโอดีเซลเพิ่มขึ้นเมื่อเทียบกับการแตกตัวแบบไม่ใช้ตัวเร่งปฏิกิริยา ค่าการเปลี่ยนและปริมาณของผลิตภัณฑ์บางส่วนที่เป็นแก๊สและส่วนที่เป็นของเหลวขึ้นกับอุณหภูมิในการเกิดปฏิกิริยาและปริมาณของตัวเร่งปฏิกิริยา อย่างไรก็ตาม ไม่มีผลต่อความเลือกจำเพาะต่อชนิดผลิตภัณฑ์ ส่วนที่เป็นแก๊สที่ได้จากปฏิกิริยาการแตกตัวของของเสียจากการผลิตไบโอดีเซลประกอบด้วย 1,3-บิวทไดอินและแก๊สคาร์บอนไดออกไซด์เป็นส่วนใหญ่ ขณะที่ส่วนที่เป็นของเหลวได้ 2-ไซโคลเพนเทน-1-โอินเป็นหลัก อย่างไรก็ตามตัวเร่งปฏิกิริยาที่ใช้แล้วในการเร่งปฏิกิริยาแบบเฟสเหลวจะไม่สามารถนำกลับมาปรับสภาพให้เหมือนใหม่ได้ เนื่องจากสารตั้งต้นที่มีสมบัติเป็นเบส การเร่งปฏิกิริยาแบบเฟสไอจึงถูกนำมาใช้เพื่อแก้ปัญหานี้ ตัวเร่งปฏิกิริยาอะลูมิเนียม-เอสบีเอ-15 ที่ใช้งานแล้วสามารถปรับสภาพเหมือนใหม่ได้ด้วยการเผาธรรมชาติ ตัวเร่งปฏิกิริยาที่ปรับสภาพเหมือนใหม่แล้วมีความว่องไว และให้ผลิตภัณฑ์ที่มีองค์ประกอบใกล้เคียงกับที่ได้จากตัวเร่งปฏิกิริยาที่ยังไม่ได้ใช้งาน

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 KEYWORDS: SBA-15 / Al-SBA-15 / CATALYTIC CRACKING / WASTE FROM
 BIODIESEL PRODUCTION

RANGSAN CHAKKASEMKIJ: CATALYTIC CRACKING OF WASTE
 FROM BIODIESEL PRODUCTION USING Al-SBA-15.

THESIS ADVISOR: DUANGAMOL NUNTASRI, Ph.D., 105 pp.

Hexagonal mesoporous silica SBA-15 was synthesized by hydrothermal method in acidic media ($\text{pH} < 1$) in the presence of commercial nonionic triblock (poly(ethylene oxide)₂₀-poly(propylene oxide)₇₀-poly(ethylene oxide)₂₀) or (PEO₂₀PPO₇₀PEO₂₀; P123) copolymer as a structure directing agent with gel composition 1.00 TEOS : 1.65×10^{-2} P123 : 6.95 HCl : 140 H₂O. The Al-SBA-15 catalysts with various Si/Al molar ratios were synthesized by stirring SBA-15 in sodium aluminate solution for 12 h. The Na⁺ of Al-SBA-15 was exchanged to H⁺ by reflux with 0.01 M NH₄Cl for 24 h. The synthesized catalysts were characterized by X-ray powder diffraction, nitrogen sorption analysis, inductively coupled plasma-atomic emission, solid state ²⁷Al-MAS-NMR and scanning electron microscopy. Catalytic cracking of waste from biodiesel production (WBP) over synthesized acidic and non-acidic SBA-15 at atmospheric pressure was investigated under different conditions. The average composition of the WBP was glycerol 37.18%, ash 6.49%, water 1.85% and matter organic non-glycerol 54.48% at pH 10.47 with the density of 1.03g/mL. The optimum condition on the WBP cracking in liquid-phase catalytic reaction is at the reaction temperature of 400°C with 10wt% catalyst amount to the WBP. When Al-SBA-15 was used as catalyst, the conversion of the WBP increases compared to that in the absence of catalyst. The conversion and yields of gas fraction and liquid fraction depend on the reaction temperature and the amount of catalyst. However, the product selectivity is not affected. The gas fraction obtained by WBP cracking mostly composes 1,3-butadiene and CO₂, whereas the liquid fraction provides 2-cyclopenten-1-one as a major liquid product. However, catalyst in liquid-phase catalytic reaction cannot be regenerated because of the alkali-starting materials. Vapour-phase catalytic reaction was considered to solve this problem. The used Al-SBA-15 can be regenerated by simple calcination. The regenerated catalyst exhibits similar activity and performs the product composition closing to the fresh one.

Field of Study: Petrochemistry and Polymer Science Student's Signature Rangsan Chakkasemkij
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LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
BJH	Barret, Joyner, and Halenda
°C	Degree Celsius
cps	Counts per second
g	Gram (s)
GC	Gas chromatography
h	Hour
ICP-AES	Inductively coupled plasma-atomic emission spectrometer
M	Molarity
MAS-NMR	Magic-angle-spinning-nuclear magnetic resonance
mg	Milligram (s)
min	Minute (s)
MONG	Matter organic non-glycerol
MS	Mass spectroscopy
ppm	Part per million
SEM	Scanning electron microscopy
TEOS	Tetraethyl orthosilicate
TPD	Temperature-programmed desorption
WBP	Waste from biodiesel production
XRD	X-ray diffraction
%	Percentage