

**MECHANISM STUDY OF HYDROCARBON PRODUCTION
FROM OXYGEN-CONTAINING C4 COMPOUNDS**



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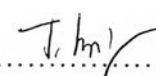
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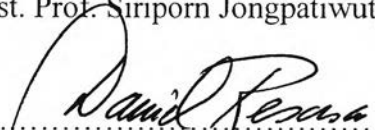
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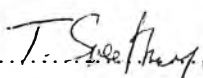

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ABSTRACT

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The mechanism of the hydrogenation of butyric acid and methyl butyrate over NiMo/Al₂O₃ and Pd/C catalysts was studied. Possible intermediates i.e. butanal and n-butanol also tested to confirm the reaction pathways. The reactions were carried out in a packed-bed reactor under temperatures of 250–350°C, pressures of 200–600 psig, H₂/feed ratio of 2.5, and LHSV of 2.0 h⁻¹. The results show that Pd/C was selective to the hydrodecarbonylation path, resulting in propane as the main product. At the same time, butane, which occurred via hydrodeoxygenation, was slightly increased with increasing reaction pressure. For NiMo/Al₂O₃, the reaction pressure significantly affects the product selectivity, as butane was mainly observed at high pressure and propane was mainly observed at low pressure. However, coupling ester, butyl butyrate was considered as the major competitive product, especially on NiMo/Al₂O₃. The intermediates found in the product were butanal and n-butanol. Moreover, condensed products produced via etherification and ketonic decarboxylation reaction which are dibutyl ether, and 4-heptanone and heptane were also observed.

บทคัดย่อ

พงษ์เทพ โลหะกิจเสถียร : การศึกษากลไกในการเกิดสารประกอบไฮโดรคาร์บอน จากสารอินทรีย์ที่มีคาร์บอน 4 อะตอมและมีออกซิเจนเป็นองค์ประกอบ (Mechanism Study of Hydrocarbon Production from Oxygen-containing C4 Compounds) อ. ที่ปรึกษา: ผศ.ดร. ศิริพร จงผาคิวุฒิ, ศ.ดร. สมชาย โอสุวรรณ และ ศ.ดร. แดเนียล อี ริชส์โก 56 หน้า

กลไกในการเกิดปฏิกิริยาไฮโดรจีเนชันของกรดบิวทิริก และ เมทิล บิวทิเรต ได้ถูกทำการศึกษาบนตัวเร่งปฏิกิริยานิกเกิลโมลิบดีนัมบนตัวรองรับอะลูมินา และ พาลาเดียมบนตัวรองรับคาร์บอน นอกจากนี้ยังใช้สารมัธยันต์ของปฏิกิริยาซึ่งก็คือบิวทานเนล และ บิวทานอลเพื่อยืนยันกลไกในการเกิดปฏิกิริยาดังกล่าว โดยทำการทดลองในปฏิกรณ์ชนิดเบดนิ่งในช่วงอุณหภูมิ 250 ถึง 350 องศาเซลเซียส ความดัน 200 ถึง 600 psig ปริมาณไฮโดรเจนต่อสารตั้งต้นโดยโมลเท่ากับ 2.5 และ LHSV เท่ากับ 2 ต่อชั่วโมง โดยจากผลการทดลองแสดงให้เห็นว่าตัวเร่งปฏิกิริยาพาลาเดียมบนตัวรองรับคาร์บอนนั้น มีการเลือกสรรต่อการเกิดปฏิกิริยาไฮโดรดีคาร์บอนิลเลชันเป็นผลให้เกิดโพรเพนเป็นผลิตภัณฑ์หลัก ในขณะที่บิวเทนซึ่งเกิดจากปฏิกิริยาไฮโดรดีออกซิจีเนชันมีการเพิ่มขึ้นเล็กน้อยเมื่อทำการเพิ่มความดันในการทำปฏิกิริยา สำหรับตัวเร่งปฏิกิริยานิกเกิลโมลิบดีนัมบนตัวรองรับอะลูมินา พบว่าความดันในการทำปฏิกริยานั้นส่งผลต่อการเลือกสรรในการเกิดสารผลิตภัณฑ์ โดยพบบิวเทนเป็นผลิตภัณฑ์หลักเมื่อทำการทดลองที่ความดันสูง แต่จะพบโพรเพนเป็นผลิตภัณฑ์หลักเมื่อทำการทดลองที่ความดันต่ำ และยังพบว่าเกิดสารประกอบเอสเทอร์ (บิวทิล บิวทิเรท) ในปริมาณมากโดยเฉพาะบนตัวเร่งปฏิกิริยานิกเกิลโมลิบดีนัมบนตัวรองรับอะลูมินา สารมัธยันต์อื่นๆที่พบในผลิตภัณฑ์ประกอบด้วยเช่น บิวทานเนล และ บิวทานอล นอกจากนี้ยังพบสารประกอบที่เกิดจากการควบแน่นที่เกิดจากปฏิกิริยาอีเทอร์ริฟิเคชันและปฏิกิริยาการเกิดสารประกอบคีโตนโดยการปลดปล่อยคาร์บอนไดออกไซด์ ซึ่งก็คือ ไดบิวทิลอีเทอร์, 4-เฮปทาโนน และเฮปเทน

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