


**SULFUR IN TIRE-DERIVED OILS AND MODIFIED CATALYSTS FOR
SULFUR REDUCTION**

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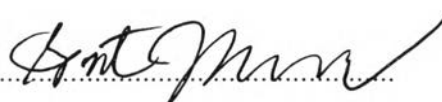
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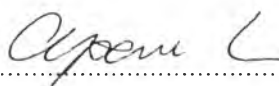


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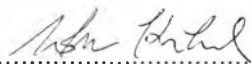
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ABSTRACT

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A number of contaminating sulfur compounds of about 1.4-1.5 wt% in tire-derived oils are a problem of not only the oil properties but also environmental regulations. This reason leads to the development of strategies for simultaneous cracking process of tire together with sulfur content reduction. The combination of catalytic pyrolysis of waste tire and desulfurization are required in order to obtain light oil with the lowest sulfur levels by using cracking and desulfurizing catalysts. The high sulfur levels in the oil products can be diminished by using a rhodium catalyst because it was found to have both cracking and desulfurization ability. In this work, Rh supported on different zeolites (KL, HY, and HBETA) were investigated for the influences of the supports. Moreover, regenerated commercial sulfided NiMoS/Al₂O₃ and fresh CoMoS/Al₂O₃ catalysts were also used as a catalyst for the pyrolysis of waste tire since they contain both acid and metal sulfide functions that could potentially benefit cracking and sulfur removal simultaneously. It was found that 0.25 wt% Rh/HBETA increased gas yield, especially the cooking gas with the lowest of liquid product, and resulted in the transformation of sulfur in oil to H₂S gas and the remaining 0.75 wt% of sulfur in pyrolysis oil. It also was observed that the introduction of Rh led to remarkable formation of mono-aromatics. The commercial hydrodesulfurization catalysts had less cracking activity than 0.25 wt% Rh/HBETA, so they gave less gas yield but high selectivity to light alkane gas product. The quality oil reached the lowest sulfur in oil (0.55 wt%) by using CoMoS/Al₂O₃ catalyst. However, the sulfur species found the most in this study were benzothiophene derivatives.

บทคัดย่อ

ภาสินี แสงอารยะกุล: กำมะถันในน้ำมันจากยางรถยนต์หมดสภาพและตัวเร่งปฏิกิริยาสำหรับลดกำมะถัน (Sulfur in Tire-Derived Oils and Modified Catalysts for Sulfur Reduction)
 อ. ที่ปรึกษา: รศ. ดร. ศิริรัตน์ จิตการคำ 120 หน้า

การเจือปนของกำมะถันจำนวนมากโดยประมาณร้อยละ 1.4-1.5 โดยน้ำหนักในน้ำมันจากยางรถยนต์ส่งผลถึงคุณภาพของน้ำมันและปัญหาสิ่งแวดล้อม ด้วยเหตุนี้จึงนำไปสู่การพัฒนาวิธีการสำหรับกระบวนการแตกพันธะของยางร่วมกับการลดปริมาณกำมะถันไปพร้อมกัน กระบวนการร่วมระหว่างการใช้ไพโรไลซิสโดยใช้ตัวเร่งปฏิกิริยาของยางรถยนต์หมดสภาพและการลดปริมาณสารกำมะถันนั้นเป็นที่ต้องการเพื่อให้ได้น้ำมันชนิดเบาที่มีระดับสารกำมะถันน้อยที่สุด โดยอาศัยตัวเร่งปฏิกิริยาที่ช่วยแตกพันธะและลดปริมาณสารกำมะถันได้ ระดับของสารกำมะถันที่สูงในน้ำมันนั้นสามารถกำจัดออกไปได้โดยอาศัยตัวเร่งปฏิกิริยาโรเดียม เนื่องจากพบว่าโลหะโรเดียมมีความสามารถทั้งการช่วยแตกพันธะและลดปริมาณสารกำมะถันได้ งานวิจัยนี้เป็นการศึกษาผลของการใช้โลหะโรเดียมร่วมกับซีโอไลต์ต่างชนิดๆ (เคแอล, เอชวาย, เอชเบต้า) เพื่อศึกษาอิทธิพลของตัวรองรับต่างชนิด นอกจากนี้ยังนำตัวเร่งปฏิกิริยาที่ใช้ในการกำจัดกำมะถันในทางการค้า 2 ประเภท ซึ่งก็คือ นิกเกิล-โมลิดินัม ที่ถูกปรับสภาพเพื่อนำกลับมาใช้ใหม่ และตัวเร่งปฏิกิริยา โคบอลต์-โมลิดินัม ชนิดซัลไฟด์บนอลูมินามาใช้ เนื่องจากตัวเร่งปฏิกิริยาเหล่านี้มีคุณสมบัติความเป็นกรดและมีสารประกอบซัลไฟด์ของโลหะซึ่งช่วยในการแตกพันธะและการกำจัดสารกำมะถันได้พร้อมกัน จากการทดลองพบว่าร้อยละ 0.25 ของโลหะโรเดียมบนเอชเบต้าสามารถเพิ่มปริมาณแก๊ส โดยเฉพาะแก๊สซัลเฟอร์ไดออกไซด์ และส่งผลต่อการเปลี่ยนรูปสารกำมะถันในน้ำมันไปเป็นแก๊สไข่เน่าและผลิตปริมาณของเหลวที่น้อยที่สุด แต่คงเหลือปริมาณกำมะถันในน้ำมันร้อยละ 0.75 โดยน้ำหนัก นอกจากนี้ยังพบว่าการใช้โลหะโรเดียมนั้นช่วยเพิ่มสาร โมโนอะโรมาติกส์อีกด้วย การใช้ตัวเร่งปฏิกิริยาไฮโดรดีซัลเฟอไรเซชันทางการค้าช่วยในการแตกพันธะในปฏิกิริยาได้น้อยกว่าตัวเร่งปฏิกิริยาที่มีร้อยละ 0.25 ของโลหะโรเดียมบนเอชเบต้า จึงให้ผลของแก๊สน้อยแต่เลือกผลิตเป็นแก๊สอัลเคนเบาได้สูง การใช้ตัวเร่งปฏิกิริยาโคบอลต์-โมลิดินัม ชนิดซัลไฟด์ บนอลูมินา สามารถลดปริมาณสารกำมะถันได้มากที่สุดถึงร้อยละ 0.55 โดยน้ำหนัก อย่างไรก็ตามสารประกอบกำมะถันที่พบมากที่สุดในการทดลองนี้เป็นอนุพันธ์ของสารเบนโซโซโรโอฟิน

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