

PROPERTIES OF NICKEL-SUPPORTED PALM  
OIL FUEL ASH (Ni-POFA) CATALYST  
PRODUCED VIA IN SITU GLYCINE-NITRATE  
COMBUSTION FOR METHANE CRACKING

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We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Science.



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## STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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Thesis submitted in fulfillment of the requirements  
for the award of the degree of  
Master of Science

College of Engineering  
UNIVERSITI MALAYSIA PAHANG

OCTOBER 2021

## ACKNOWLEDGEMENTS

In the name of Allah, the Most Beneficent and the Most Merciful. All praises to Allah the Almighty for giving me the strengths, guidance and patience in completing my master research and this thesis

First and foremost, my sincere thanks and utmost appreciation to my dedicated supervisor, Dr. Asmida Ideris for her detailed explanation and comments in every stage of my research work, provide me continuous assistance and encouragement, and invaluable advice in completing my master research. Besides, I would like to thank to my co-supervisor, Dr. Mazni Ismail for her enthusiasm, motivation and immense knowledge significantly assisted me in my research work. Thank you very much for the unending help throughout of my master research.

My special acknowledgement goes to the administrative and technical staff of Universiti Malaysia Pahang (UMP) for giving me full support in the success of my experimental work. This research would not have been possible without their contributions.

My deepest gratitude goes to my beloved father and mother, Hanifa bin Awang and Zahrah binti Ahmad for their endless love, prayers and tolerance. To my wonderful younger sister and younger brother, thank you for your persevering support and encouragement. I would like to express my genuine gratitude to my friends and colleagues especially in the Department of Chemical Engineering for their motivation, encouragement and moral support. Last but not least, I would like to thank to all the people who have helped me throughout my research, directly or indirectly, your contribution shall not be forgotten.

## ABSTRAK

Peretakan metana merupakan kaedah alternatif untuk penghasilan gas H<sub>2</sub> dengan sifar pembebasan CO<sub>x</sub> dan pembebasan gas rumah hijau yang rendah. Sisa pertanian, abu kelapa sawit (POFA) berpotensi dijadikan sebagai bahan sokongan pemangkin untuk peretakan metana kerana ia mengandungi kandungan silika (SiO<sub>2</sub>) yang tinggi. Faktor-faktor mempengaruhi ciri pemangkin telah dikaji dalam kajian ini, bertujuan untuk menghasilkan pemangkin Ni-POFA dengan prestasi dan kestabilan yang baik. Awalnya, ciri-ciri POFA sebagai bahan sokongan pemangkin telah dinilai dalam proses pra-rawatan POFA dimana kesan penggunaan pelarut yang berbeza (HCl, asid sitrik dan NaOH) dan teknik pra-rawatan POFA (adukan lazim dan ultra-sonik) telah disiasat. Sintesis pemangkin baharu; pembakaran glisin-nitrat (in situ GNP) juga telah diterokai. Akhirnya, kesan kandungan Ni (5–20 wt.%) dan halaju ruang gas setiap jam (GHSV) (5,000–25,000 mL/g.h) juga telah disiasat. Peretakan mangkin metana menggunakan pemangkin Ni-POFA dinilai pada 550°C selama 6 jam. Pencirian POFA dan pemangkin Ni-POFA telah dilakukan menggunakan XRF, XRD, luas permukaan BET, H<sub>2</sub>-TPR, penyerapan kimia H<sub>2</sub>, FESEM dan TGA. Hasil kajian pra-rawatan, kandungan SiO<sub>2</sub> dalam POFA terawat telah meningkat daripada 42 kepada 72% dirawat menggunakan larutan asid sitrik. Pemangkin Ni-POFA yang dihasilkan dari POFA dirawat menggunakan teknik ultra-sonik menunjukkan luas permukaan BET yang lebih besar (12.2 m<sup>2</sup>/g) berbanding dengan yang menggunakan teknik adukan lazim (9.2 m<sup>2</sup>/g). POFA dirawat dengan menggunakan larutan asid sitrik dan teknik ultra-sonik menghasilkan pemangkin Ni-POFA dengan mangkin baik dalam peretakan metana (71% penukaran CH<sub>4</sub> awal dan 4.2% penghasilan gas H<sub>2</sub>). Sementara itu, bagi kaedah penyediaan pemangkin, Ni-POFA menggunakan kaedah in situ GNP telah menunjukkan prestasi yang baik dalam peretakan metana, menghasilkan penukaran CH<sub>4</sub> awal sebanyak 60% dan gas H<sub>2</sub> yang wajar sebanyak 8.7%. Ini telah dikaitkan dengan interaksi Ni pada sokongan POFA yang kuat, dan serakan zarah Ni yang baik dalam pemangkin Ni-POFA (GNP) sebagaimana dibuktikan oleh analisis H<sub>2</sub>-TPR dan penyerapan kimia H<sub>2</sub>. Walaupun begitu, kadar penurunan lebih tinggi dalam penukaran CH<sub>4</sub> telah berlaku pada pemangkin Ni-POFA (GNP) berbanding pemangkin yang dihasilkan menggunakan kaedah impregnasi (Ni-POFA (Imp)). Adalah dicadangkan bahawa pemangkin Ni-POFA (GNP) bukan sahaja aktif terhadap penghasilan gas H<sub>2</sub> tetapi juga dalam pembentukan karbon. Jenis pembentukan karbon juga berbeza mengikut kaedah penyediaan pemangkin di mana jenis karbon filamen telah didapati terbentuk pada permukaan pemangkin Ni-POFA (GNP) manakala jenis karbon enkapsulasi telah didapati terbentuk pada permukaan pemangkin Ni-POFA (Imp). Bagi kesan kandungan Ni, 15 wt.% adalah kandungan Ni yang optimum pada pemangkin Ni-POFA. Tambahan itu, kandungan Ni dalam Ni-POFA, telah mempengaruhi pembentukan dimensi karbon filamen pada pemangkin Ni-POFA. Akhirnya, pemangkin Ni-POFA telah menunjukkan prestasi bermangkin terbaik, penukaran CH<sub>4</sub> awal tertinggi sebanyak 87% dan penghasilan H<sub>2</sub> awal sebanyak 27% pada GHSV 7,000 mL/g.h. Kesimpulannya, POFA telah menunjukkan potensi baik sebagai bahan sokongan pemangkin Ni. Kaedah penyediaan in situ GNP dalam kajian ini telah berjaya meningkatkan prestasi bermangkin Ni-POFA bagi peretakan metana dalam penghasilan gas H<sub>2</sub>.

## ABSTRACT

Methane cracking is an alternative route for H<sub>2</sub> production with zero CO<sub>x</sub> emission and low GHGs emissions. Palm oil fuel ash (POFA) is an agricultural waste and has a potential to be developed as a catalyst support for methane cracking due its high silica (SiO<sub>2</sub>) content. In this study, factors which influence catalyst properties have been explored, aiming for Ni-POFA catalyst with excellent performance and stability. Initially, properties of POFA as catalyst support has been evaluated in POFA pre-treatment where the effects of various solvents (HCl, citric acid, and NaOH) and pre-treatment techniques (conventional stirring and ultra-sonication) have been investigated. A new preparation method for Ni-POFA; in situ glycine-nitrate combustion process (in situ GNP) also has been explored. Finally, effects of Ni loading (5–20 wt.%) and gas hourly space velocity (GHSV) (5,000–25,000 mL/h.g) have been investigated. Catalytic performance of Ni-POFA catalyst was evaluated for methane cracking at 550°C for 6 hrs. The POFA and Ni-POFA catalyst were characterized using XRF, XRD, BET surface area, H<sub>2</sub>-TPR, H<sub>2</sub> pulse chemisorption, FESEM and TGA. From the results, SiO<sub>2</sub> content in the POFA has been improved from 42 to 72% with citric acid pre-treatment. Ni-POFA catalyst produced with POFA treated using ultra-sonication technique had a larger BET surface area (12.2 m<sup>2</sup>/g) compared to one with POFA treated using conventional stirring technique (9.2 m<sup>2</sup>/g). Both citric acid solution and ultra-sonication technique were found to be the best solvent and technique for POFA pre-treatment giving the Ni-POFA a reasonable catalytic performance in methane cracking (66% of initial CH<sub>4</sub> conversion and 4.2% of initial H<sub>2</sub> yield). Meanwhile in the catalyst preparation study, Ni-POFA catalyst prepared using in situ GNP method (Ni-POFA (GNP)) has exhibited a good catalytic performance with an initial CH<sub>4</sub> conversion of 60% and 8.7% of initial H<sub>2</sub> yield. This is attributed to strong interaction between Ni and POFA, and high Ni metal dispersion in Ni-POFA (GNP) as evidenced by H<sub>2</sub>-TPR and H<sub>2</sub>-chemisorption analysis. Nevertheless, a higher degradation rate of CH<sub>4</sub> conversion was observed in Ni-POFA (GNP) compared to one produced using impregnation (Ni-POFA (Imp)). It is suggested that Ni-POFA catalyst synthesized using in situ GNP was not only active for H<sub>2</sub> production but also for carbon formation. Type of carbon formed was also varied upon the catalyst preparation method when filamentous-types of carbon was found deposited on the Ni-POFA (GNP) while the Ni-POFA (Imp) was covered by the encapsulating carbon. For the effect of Ni loading, 15 wt.% was found to be the optimal Ni loading for Ni-POFA catalyst. Additionally, the Ni loading significantly influenced the dimension of filamentous carbons available on the Ni-POFA surface. Finally, Ni-POFA gave the highest catalytic performance with 87% initial CH<sub>4</sub> conversion and 27% initial H<sub>2</sub> yield using 7,000 mL/g.h GHSV. As a conclusion, POFA exhibits a good potential as a catalyst support for Ni. POFA pre-treatment and in situ GNP preparation have successfully improved the catalyst properties, thus enhanced the catalytic performance of Ni-POFA catalyst in methane cracking for hydrogen production.

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