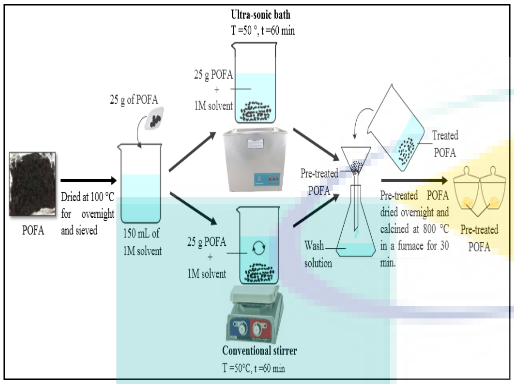
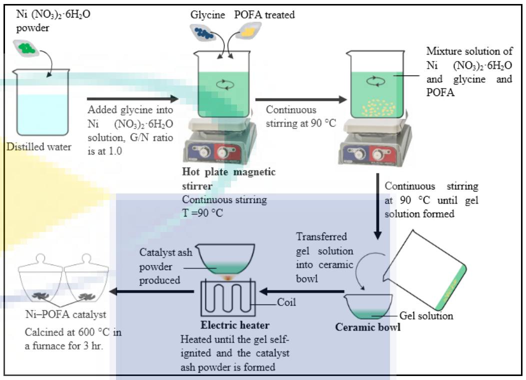
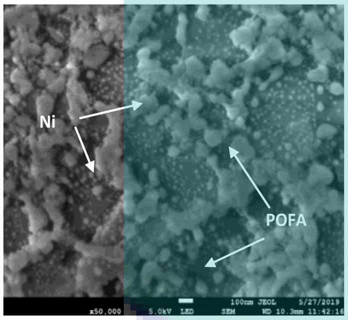
# TEMPLATE
## BUKU PROFIL PENYELIDIKAN SKIM GERAN PENYELIDIKAN GERAN UNIVERSITI JANGKA PENDEK / GERAN DALAM UMP



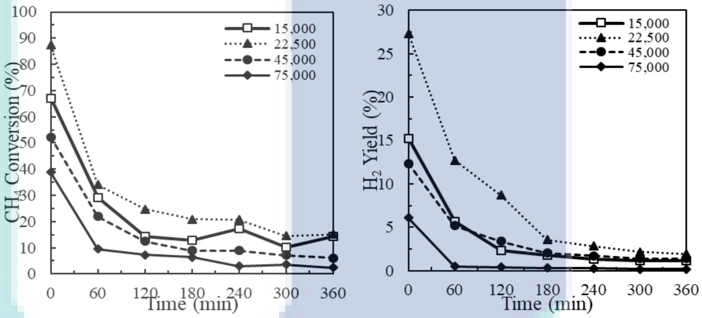
Pre-treatment of POFA



Catalyst synthesis via in situ glycine nitrate combustion (in situ GNP)



Ni-POFA catalyst



$CH_4$ conversion and $H_2$ yield from methane cracking

# METAL-SUPPORT INTERACTION OF NI-SUPPORTED PALM OIL FUEL ASH CATALYST PRODUCED FROM SELF-COMBUSTION TECHNIQUE FOR METHANE CRACKING

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Heterogenous catalyst synthesis and characterization; Hydrogen production

## ABSTRACT (120 words)

Methane cracking is an excellent route for CO-free $H_2$ production. During methane cracking, Ni-supported catalysts synthesized using conventional impregnation method are usually suffered from non-uniform distribution and agglomeration thus affected its stability. A self-combustion catalyst preparation technique; in situ glycine-nitrate combustion process (in situ GNP) has been explored with the aim of producing metal-supported catalysts with strong metal-support interaction, thus highly dispersed catalyst. In the meantime, an approach of utilizing biomass wastes for catalytic purposes seems to be promising. In this work, palm oil fuel ash (POFA) has been explored as a catalyst support in methane cracking due to its high $SiO_2$ content. Ni catalyst supported on palm oil fuel ash (Ni–POFA) has been prepared using in situ GNP and its catalytic activity of the catalysts was evaluated for methane cracking at 550°C. Effects of pre-treatment, catalyst preparation method, Ni loading and gas-space hour velocity (GHSV) have been investigated and POFA and Ni–POFA catalysts characterizations were performed using XRF, XRD, BET, FESEM, TGA and $H_2$-TPR. Pre-treatment has improved $SiO_2$ composition in POFA from 42.4 to 72.0%. A decent $CH_4$ conversion achieved by Ni–POFA catalyst produced using POFA treated with citric acid can be ascribed to high $SiO_2$ content, reasonable surface area, and moderate POFA porous structure. For catalyst preparation, Ni–POFA produced from in situ GNP has better $H_2$ yield than one produced using impregnation. High Ni dispersion has provided more availability of Ni active sites on POFA support, thus resulted in higher $H_2$ yield. Additionally, the catalyst preparation method influenced the morphology of the catalyst and the type of carbon formed on the spent Ni–POFA catalysts. At the optimum GHSV of 22,500 mL/g.h,15 wt.% Ni–POFA catalyst offered the highest catalyst stability with highest initial $CH_4$ conversion and $H_2$ yield of 87.0% of and 27.0%, respectively. As a conclusion, this project has successfully produced a stable Ni catalyst supported on palm oil fuel ash (Ni–POFA) with a decent catalytic activity for methane cracking process.

## 1. INTRODUCTION

Methane cracking is one of the hydrogen production technologies that is sustainable for hydrogen economy since it produces hydrogen with zero carbon dioxide emission and has a great potential in reducing greenhouse gases [1]. Methane cracking is a thermo-catalytic decomposition process of methane, $CH_4$ which produces carbon (C) and hydrogen gas ($H_2$) without producing carbon dioxide ($CO_2$). The increasing interest amongst researchers towards methane cracking is due to high methane conversion, the easiness of carbon to be sequestrated in a stable solid formed, and its environmental feasibilities [2].

Nickel, Ni catalyst has been widely applied in various chemical reactions such as hydro-treating, hydro-cracking and hydro-processing in oil refineries industry [3]. Ni catalyst is also used for hydrogen production in methane cracking process. It has been commonly applied by researchers for methane cracking due to its price and availability [4]. Moreover, Ni catalyst also has been proven as a very active and stable catalyst for methane cracking process within the temperature range of 500-700 ºC [5].

In metal-supported catalysts, catalyst support is the one responsible to maintain the dispersion of active metal particles and promotes stability against carbon deposition [6]. Highly dispersed active particles on the support is the main reason for high catalytic stability in methane cracking [7]. This metal dispersion is dependent on the surface interaction between metal and support established during catalyst preparation. The strong metal-support interaction can prevent the migration of Ni particles hence control the size of Ni ensembles. Hence, high dispersion of Ni particles on the support is attributed to the strong interaction between Ni and support of the catalyst [8]. In short, the synergism between the metal and the support is crucial in order to stabilize the active phase and reduce the rate of carbon deposition [9]. This metal-support interaction is highly influenced by catalyst preparation method [10].

Catalyst preparation method is a crucial factor which controlling the metal crystallite size, catalyst dispersion and distributions for excellent catalytic performance in methane cracking. Impregnation is a conventional method for catalyst preparation yet with several drawbacks. The morphology of catalyst obtained is large agglomerates of particle size, formation of higher crystallite size of metal oxides, uneven distributions of impregnant, and less metal dispersion onto the support [11]. In situ glycine-nitrate combustion synthesis (in situ GNP) of metal-supported catalysts involved the combustion reaction between the metal nitrates and glycine with the presence of the supported catalyst [3, 12, 13]. The utilization in situ GNP for preparation of metal-supported catalysts involved the combination of impregnation and solution combustion synthesis [3]. In situ GNP has become an attractive synthesis method for metal–supported catalysts as it is rapid and simple process and producing catalysts with high dispersion, high surface area and excellent catalytic activity [3, 12, 13, 14].

Recently, there has been a great interest in utilizing agricultural wastes such as palm oil fuel ash (POFA) in catalytic reactions in order to make used of their potentials while minimizing the manufacturing costs [15]. Since Malaysia is one of the world's largest producers and exporters of palm oil, POFA is abundantly produced from the combustion of palm oil biomass in the palm oil industries. Malaysian Palm Oil Board (MPOB) has reported that approximately 5% of POFA produced due to the combustion of husk and shells of palm kernel in the boiler for steam production [16]. Occasionally, POFA is disposed to landfill and the accumulation of this waste has led to the environmental pollution problems in the palm oil industries. Known for its high amount of $SiO_2$ [17], POFA exhibits a potential to be developed as a catalyst support for methane cracking.

The objectives of this project are: (1) to evaluate the effect of pre-treatment on the physical properties of palm oil fuel ash (POFA); (2) to examine the metal-support interaction of Ni-supported POFA catalyst produced from in-situ self-combustion process; and (3) to assess the catalytic performance and carbon deposition affinity of Ni-supported POFA catalyst in methane cracking.Thus, the focus of this research is on the improvement of POFA as a catalyst support aiming for high silica content with large surface area and high porosity. The performance of Ni-catalyst supported on POFA has been evaluated for methane cracking and the interaction between Ni-catalyst and POFA support has been investigated upon catalyst preparation method, Ni loading and gas-space hour velocity (GHSV).

## 2. RESEARCH METHODOLOGY

The work in the research started with drying and sieving process of POFA. During pre-treatment stage, effects of solvent and pre-treatment technique on the properties of POFA were investigated. POFA was then characterized using X-Ray fluorescence (XRF) spectrometer for its chemical composition and $N_2$ adsorption BET isotherm for the surface area and pore diameter size. POFA with high $SiO_2$ composition and high surface area was aimed for the catalyst support and further used for preparation of Ni supported on POFA (Ni–POFA) catalyst. The effects of solvent and pre-treatment technique on POFA employed as support in the Ni-based catalyst were evaluated in methane cracking. Pre-treatment process of palm oil fuel ash (POFA) is shown in Figure 2.1.

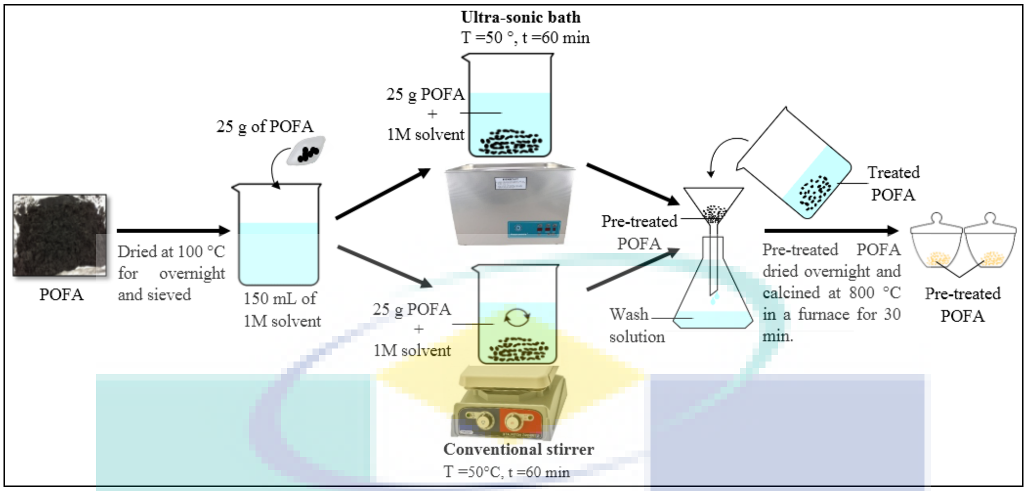

**Figure 2.1** Pre-treatment process of palm oil fuel ash (POFA)

Effect of catalyst preparation method on Ni-POFA was further investigated using two different techniques; in situ glycine-nitrate combustion and a conventional impregnation method. The properties Ni-POFA catalyst produced were characterized using X-ray diffraction (XRD) analysis, $N_2$ adsorption BET isotherm, field emission scanning electron microscopy (FESEM), thermoravimetric analysis (TGA) and $H_2$-TPR. Ni-POFA catalyst with high BET surface area, high Ni dispersions was aimed. The catalytic activity of Ni-POFA catalysts prepared using in situ glycine-nitrate combustion (in situ GNP) and impregnation method was observed in methane cracking. Preparation of Ni–POFA catalyst using in situ glycine-nitrate combustion method is illustrated in Figure 2.2.

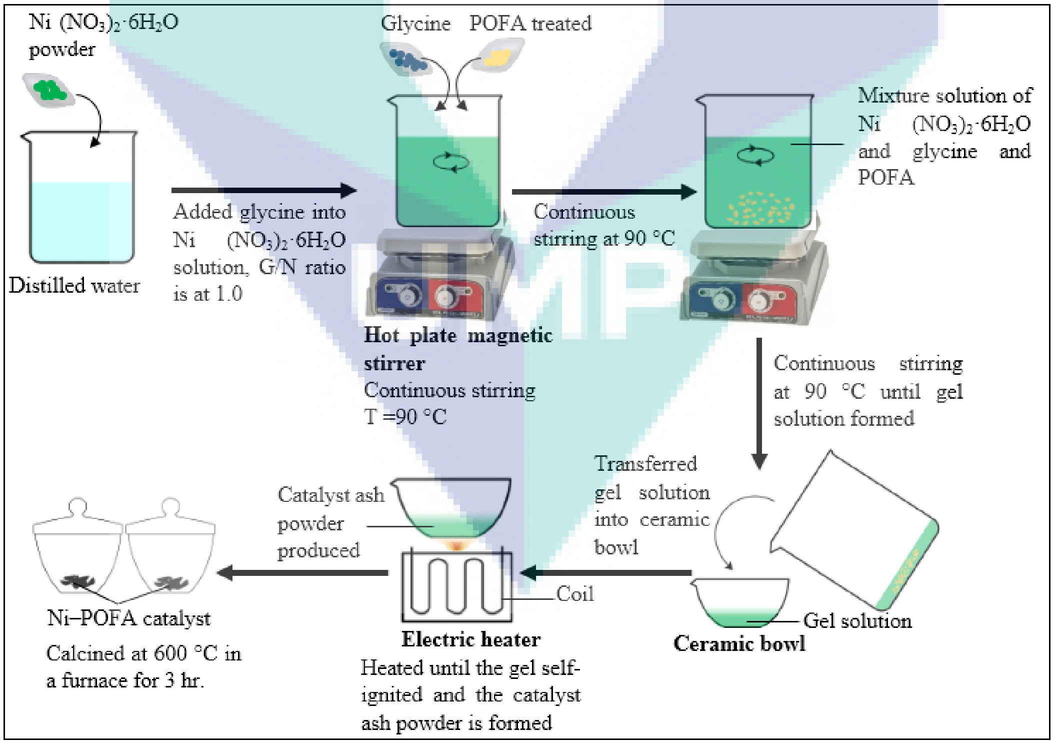

**Figure 2.2** Preparation of Ni–POFA catalyst using in situ glycine-nitrate combustion method (in situ GNP)

The catalytic performance of Ni–POFA catalysts was evaluated via methane cracking process for $H_2$ yield and methane conversion. The catalytic activity of Ni–POFA catalyst was explored upon Ni loading and gas space hour velocity (GHSV). Ni–POFA catalyst with an optimum Ni loading was further used for the evaluation at different gas space hour velocity (GHSV). Methane cracking reaction was performed at 550 °C for 6 hr. The product gas compositions were analysed using an offline gas chromatography (Agilent 7890B, USA) equipped with dual thermal conductivity detector (dual TCD) (Figure 2.3). Finally, carbon deposited on the catalyst surface of spent Ni–POFA was analyzed using field emission scanning electron microscopy (FESEM), x-ray diffraction (XRD) analysis and thermogavimetry analysis (TGA). Overall workflow of the experimental works for this project is provided in Appendix A.

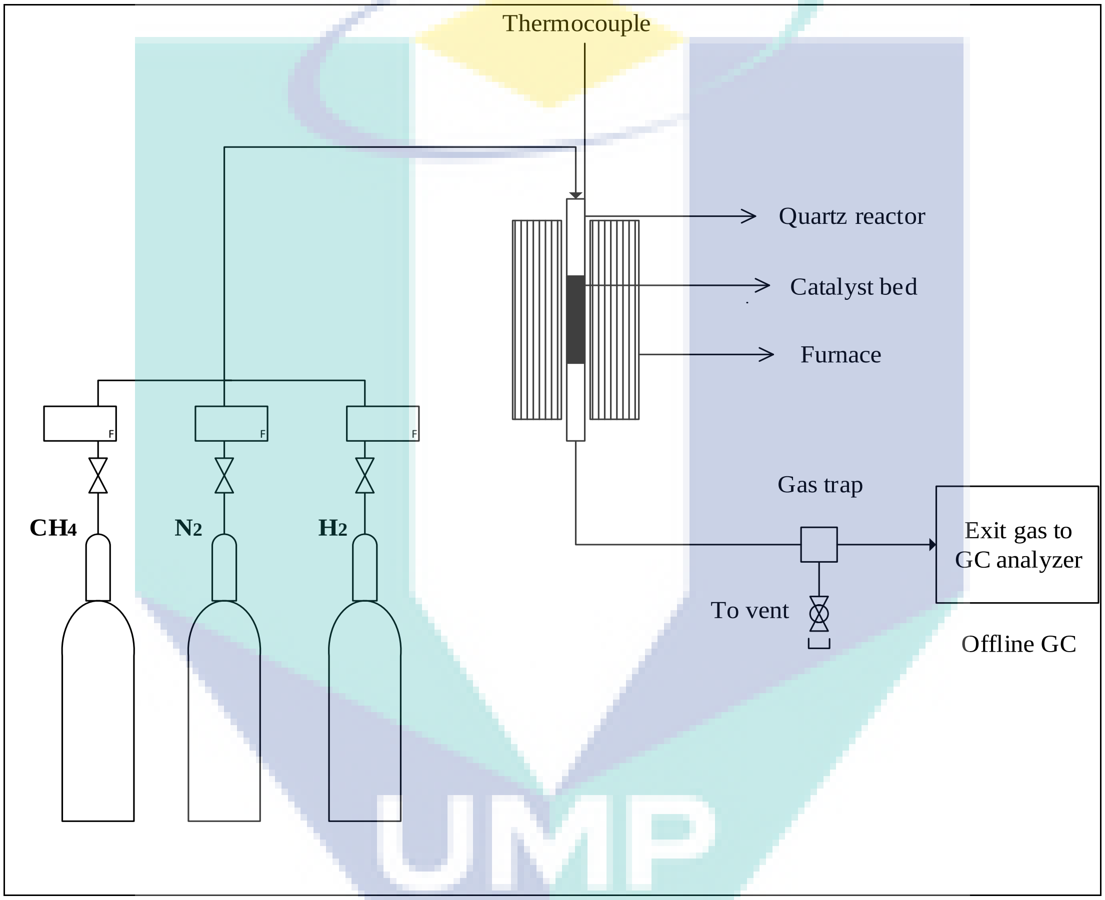

**Figure 2.3** Experimental setup of methane cracking for Ni-POFA catalyst

## 3. FINDINGS

In POFA pre-treatment, acid solution was more effective in improving the $SiO_2$ content in treated POFA as compared to the basic solution. POFA treated using acid solution also has better surface area properties than the one pre-treated using basic solution. Citric acid solution was the best solvent for POFA pre-treatment with the highest $SiO_2$ amount and the highest removal of impurities. POFA pre-treatment with citric acid has successfully removed the impurities, leaving the Ni–POFA catalyst with NiO and $SiO_2$ quartz peaks only. The pretreatment has improved the crystallinity of quartz $SiO_2$ in the Ni–POFA catalyst and thus POFA treated with citric acid was further utilized for catalyst support in this work. Ni–POFA catalyst produced using POFA treated with citric acid solution exhibited the highest initial $CH_4$ conversion of 71.0% before it was decreased over time and reached a stable value at 29.0%. Ni-POFA/citric acid catalyst produced 4.2% $H_2$ yield at before it was gradually decreased over time to 1.7% (Figure 3.1).

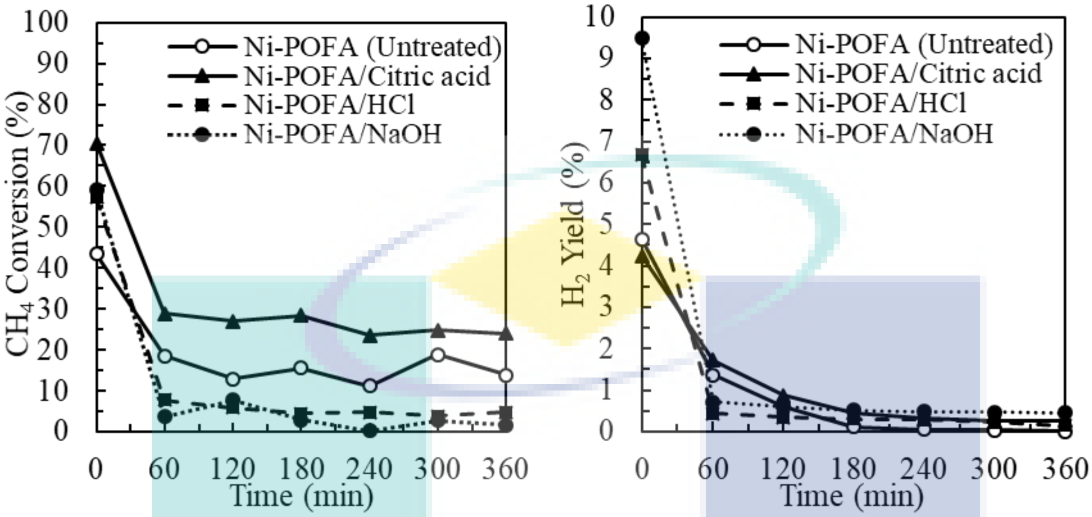

**Figure 3.1** $CH_4$ conversion and $H_2$ yield during methane cracking for Ni–POFA catalysts produced using POFA treated with NaOH, HCl and citric acid solutions.

Effect of pre-treatment techniques; ultra-sonication and conventional stirring has been discussed and Ni–POFA catalyst prepared using POFA pre-treated with ultra-sonication showed the highest initial $CH_4$ conversion of 71.0% and then remained stable at 26.0% over reaction time. Ni–POFA catalysts using untreated POFA and one treated using conventional stirring on the other hand were only able to achieved up to 15.0% and 12.0% conversions, respectively (Figure 3.2). Ultra-sonication has resulted in the smaller particles of POFA support compared to the support treated using conventional stirring. Large pore diameter of POFA support was found for Ni–POFA catalyst with POFA treated conventional stirring given lower BET in POFA treated with conventional stirring (Figure 3.3).

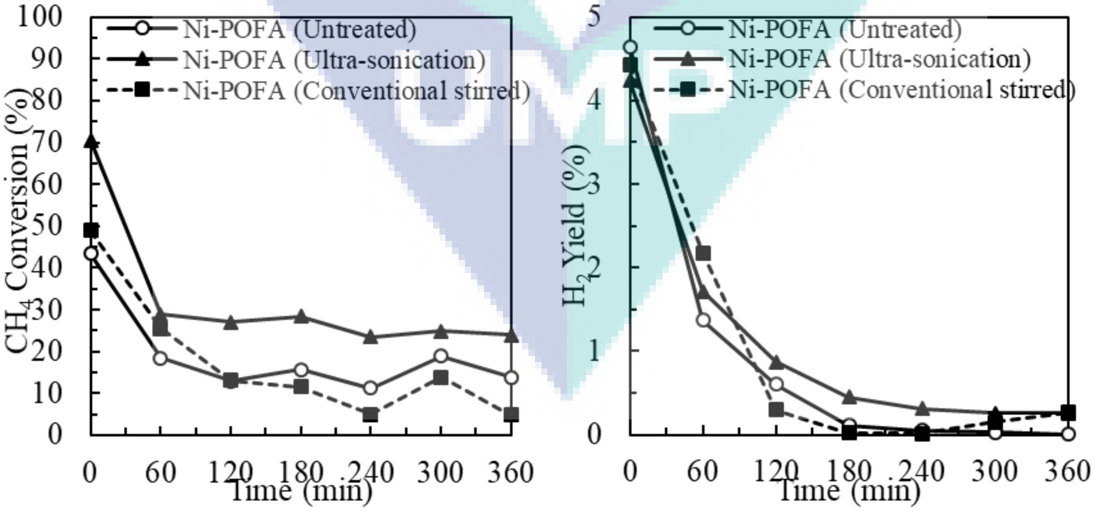

**Figure 3.2** $CH_4$ conversion and $H_2$ yield during methane cracking at 550 °C for Ni–POFA catalysts produced with POFA treated via conventional stirring and ultra-sonication techniques.

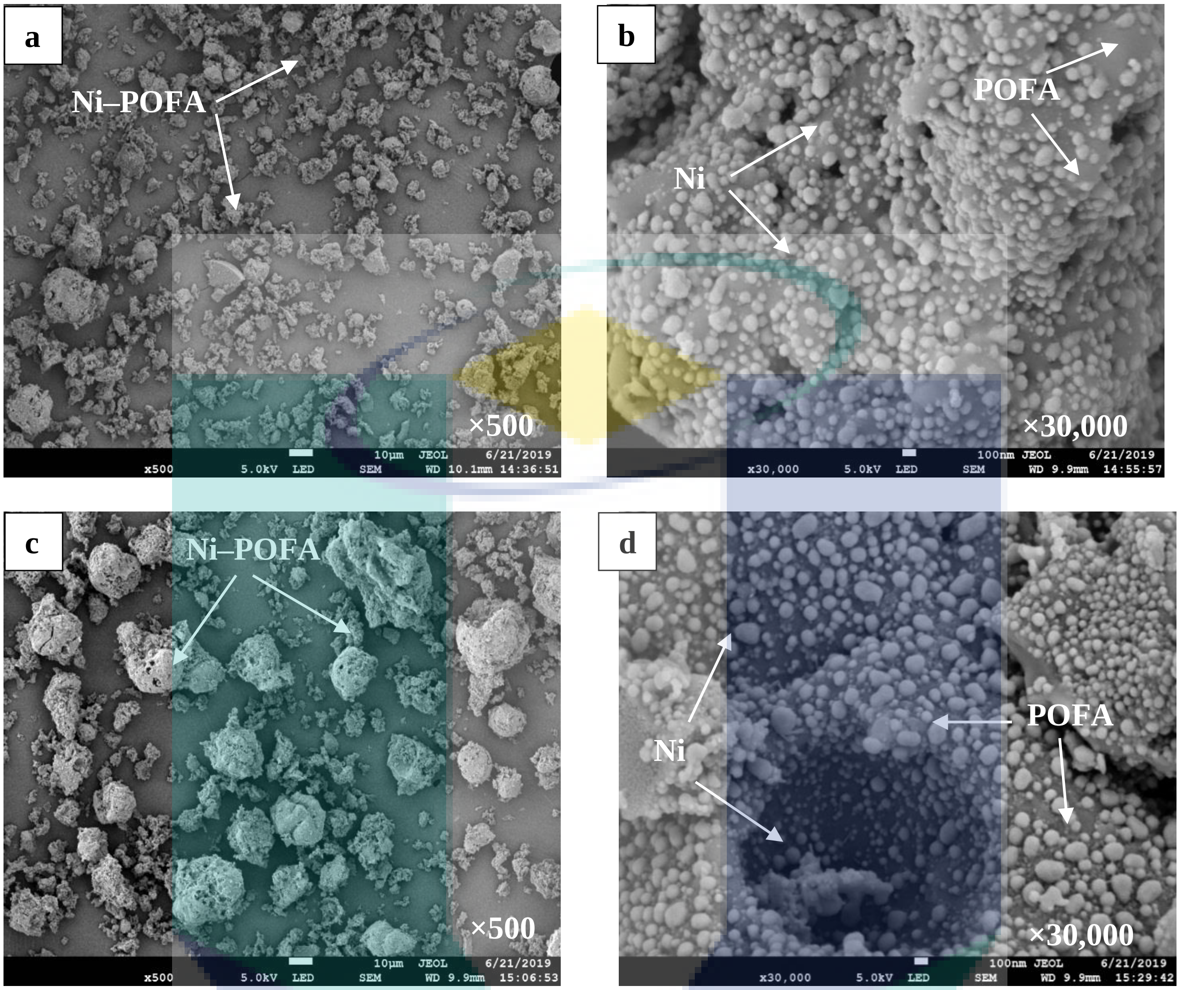

**Figure 3.3** FESEM micrographs of Ni–POFA catalysts produced using POFA treated via a-b) ultra-sonication and c-d) conventional stirred techniques

Effect of catalyst preparation method has been explored to improve the dispersion of active metal particles on support thus enhance the activity of Ni–POFA catalyst toward methane cracking reaction. The cystalline intensity of Ni phase for Ni–POFA synthesized using in situ glycine nitrate combustion was slightly lower compared to the one produced using impregnation (Figure 3.4). Ni–POFA synthesized using in situ glycine-nitrate combustion was found to a better Ni dispersion over the surface of POFA compared to the one synthesized using impregnation method. $CH_4$ conversion of Ni–POFA catalysts synthesized using in situ glycine-nitrate combustion (In situ Ni–POFA) dropped drastically and reached stability at only 8.8% over the reaction time. Meanwhile, $CH_4$ conversion for Ni–POFA catalysts synthesized using impregnation (Im Ni–POFA) was maintained at 26.0%. The degradation rate of $CH_4$ conversion for Ni–POFA synthesized using in situ GNP is more significant than the one produced using impregnation. Nevertheless, better $H_2$ yield in the In situ Ni–POFA can be attributed to high dispersion of Ni metal as evidenced by its low crystallinity of Ni phase and low Ni crystallite size. High Ni dispersion provided more availability of Ni active sites on POFA support, thus resulted in higher $H_2$ yield in Ni–POFA synthesized using in situ glycine-nitrate combustion (Figure 3.5).

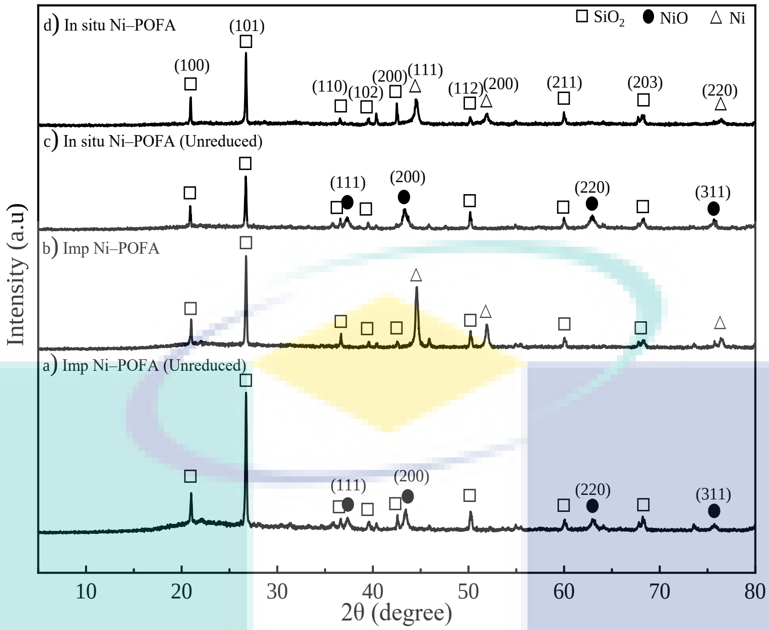

**Figure 3.4** XRD patterns of unreduced and reduced samples of Ni–POFA catalysts synthesized using a−b) Impregnation and c−d) In situ glycine-nitrate combustion

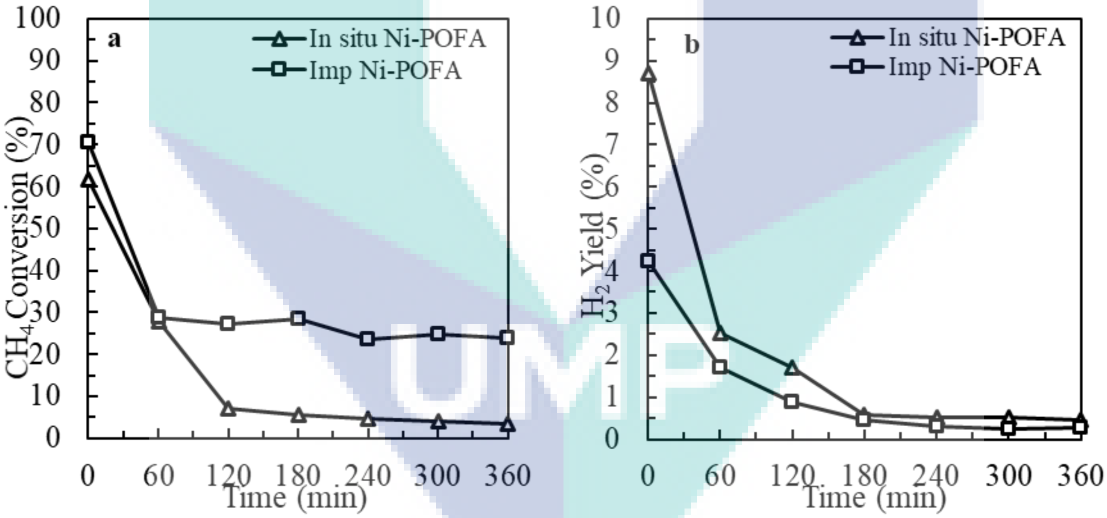

**Figure 3.5** a) $CH_4$ conversion and b) $H_2$ yield for Ni–POFA catalysts synthesized using impregnation (Imp Ni–POFA) and in situ glycine-nitrate combustion (In situ Ni–POFA) during methane cracking at 550 °C.

An accumulation of filamentous-types of carbon was found deposited on the surface of Ni–POFA synthesized using in situ glycine-nitrate combustion, which could be the main reason the higher degradation rate of $CH_4$ conversion of In situ Ni–POFA catalyst compared to Im Ni–POFA. In situ Ni–POFA was not only active for $H_2$ production but also in carbon formation. Meanwhile, encapsulating carbon was formed on the spent Ni–POFA catalysts synthesized using impregnation method, covering most of the surface of large agglomerate of Ni particles (Figure 3.6). This suggests that catalyst preparation method influenced the morphology of the catalyst and the type of carbon formed on the spent Ni–POFA catalysts. From the TGA analysis, more carbon has been deposited on the In situ Ni–POFA compared to the Imp Ni–POFA catalyst. In summary, in situ glycine-nitrate combustion employed for the synthesis of Ni–POFA catalyst has provided Ni–POFA with high Ni dispersion, thus resulted in an active catalyst with higher $H_2$ yield than one prepared using impregnation.

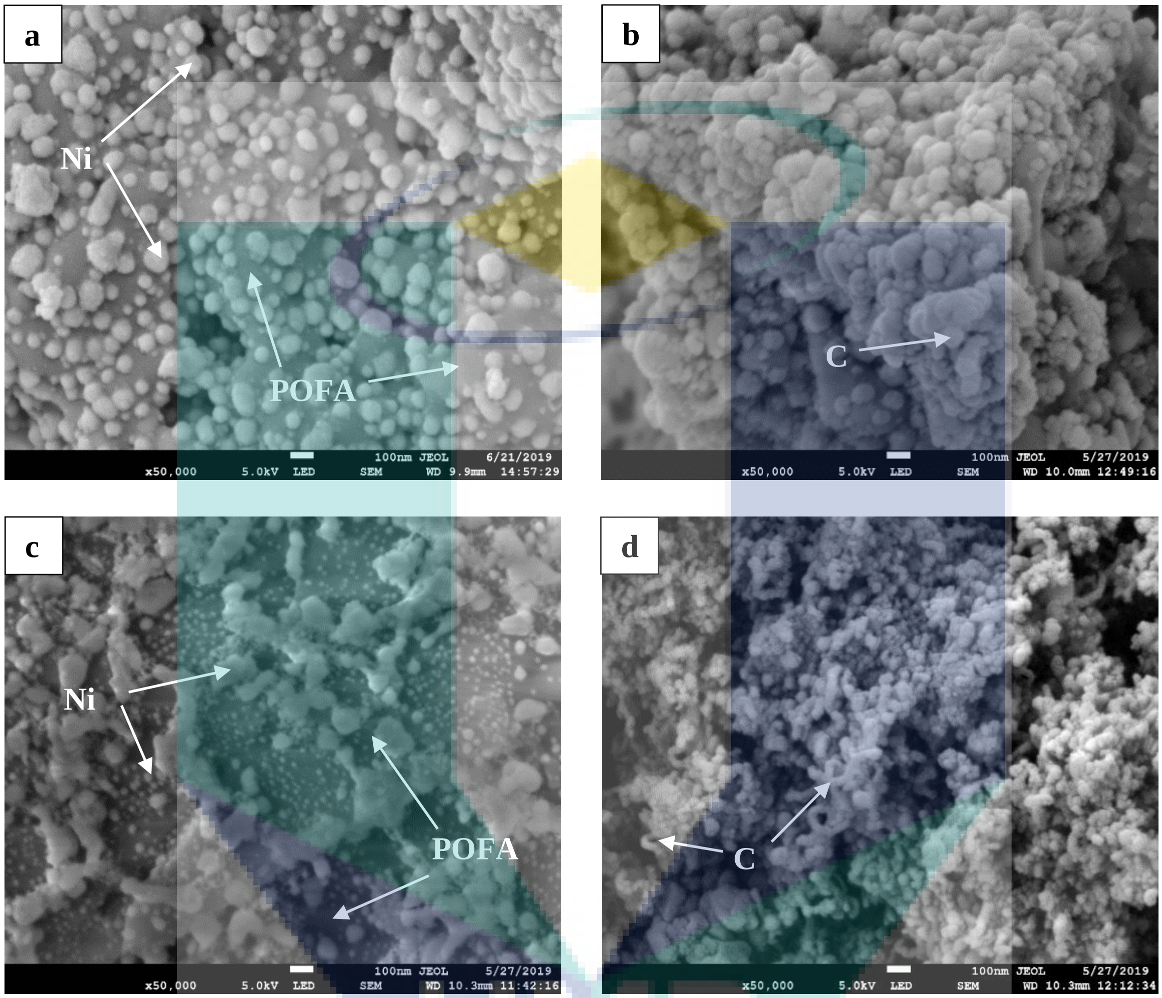

**Figure 3.6** FESEM micrographs of fresh and spent Ni–POFA catalysts synthesized using a-b) impregnation and c-d) in situ glycine-nitrate combustion method.

Ni-POFA synthesized using in situ glycine-nitrate combustion was further evaluated for effect of Ni loading. 15 wt.% of Ni was found to be an optimal Ni loading for Ni–POFA catalyst synthesized using in situ glycine-nitrate combustion (Figure 3.7). 15 wt.% Ni–POFA catalyst has demonstrated the most stable CH4 conversion and an excellent catalytic performance with an exceptional $H_2$ yield. Based on XRD and Ni crystallite size, the reasonable performance of 15 wt.% Ni–POFA catalyst is attributed to high Ni dispersion on POFA support surface and the presence of adequate amount of Ni active phase in Ni–POFA catalyst.

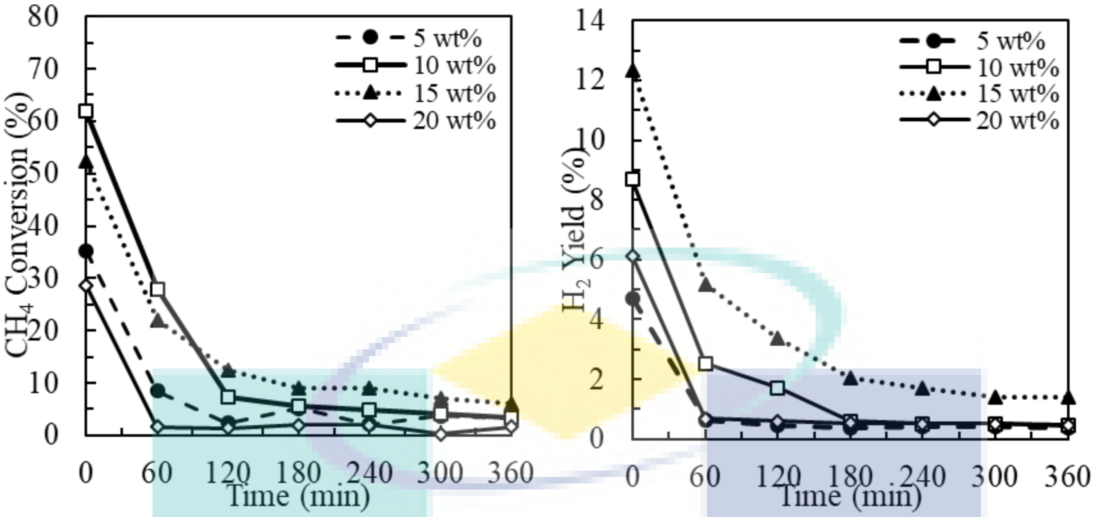

**Figure 3.7** a) $CH_4$ conversion and b) $H_2$ yield for Ni–POFA catalysts synthesized using in situ glycine-nitrate combustion at different Ni loading; 5 wt%, 10 wt%, 15 wt% and 20 wt% during methane cracking at 550 °C.

The formation of filamentous-type carbons can be clearly observed on all spent Ni–POFA catalysts at various catalyst loading. However, the filamentous carbons grown on the surface of the spent catalysts were found to be different in their lengths and diameters (Figure 3.8). In overall, the average diameter of filamentous carbons increased with the increase of Ni loading employed in the Ni–POFA catalyst, indicating that Ni loading influenced the growth of filamentous carbons on the active sites of the catalyst.

In the attempt to maximize the yield of hydrogen from the Ni–POFA catalyst, effect of GHSV on the catalytic performances has been further explored to obtain the optimum operating condition of methane cracking for the synthesized 15 wt.% Ni–POFA catalyst. Optimum GHSV for methane cracking has been achieved at 22,500 mL/g.h when as high as 87.0% and 27.0% were attained for initial $CH_4$ conversion and $H_2$ yield, respectively (Figure 3.9). GHSV at 22,500 mL/g.h has provided enough contact time between $CH_4$ gas and Ni active sites in the Ni–POFA catalyst. Furthermore, at GHSV=22,500 mL/g.h, the production of $H_2$ reached its highest stable value at 5.3%.

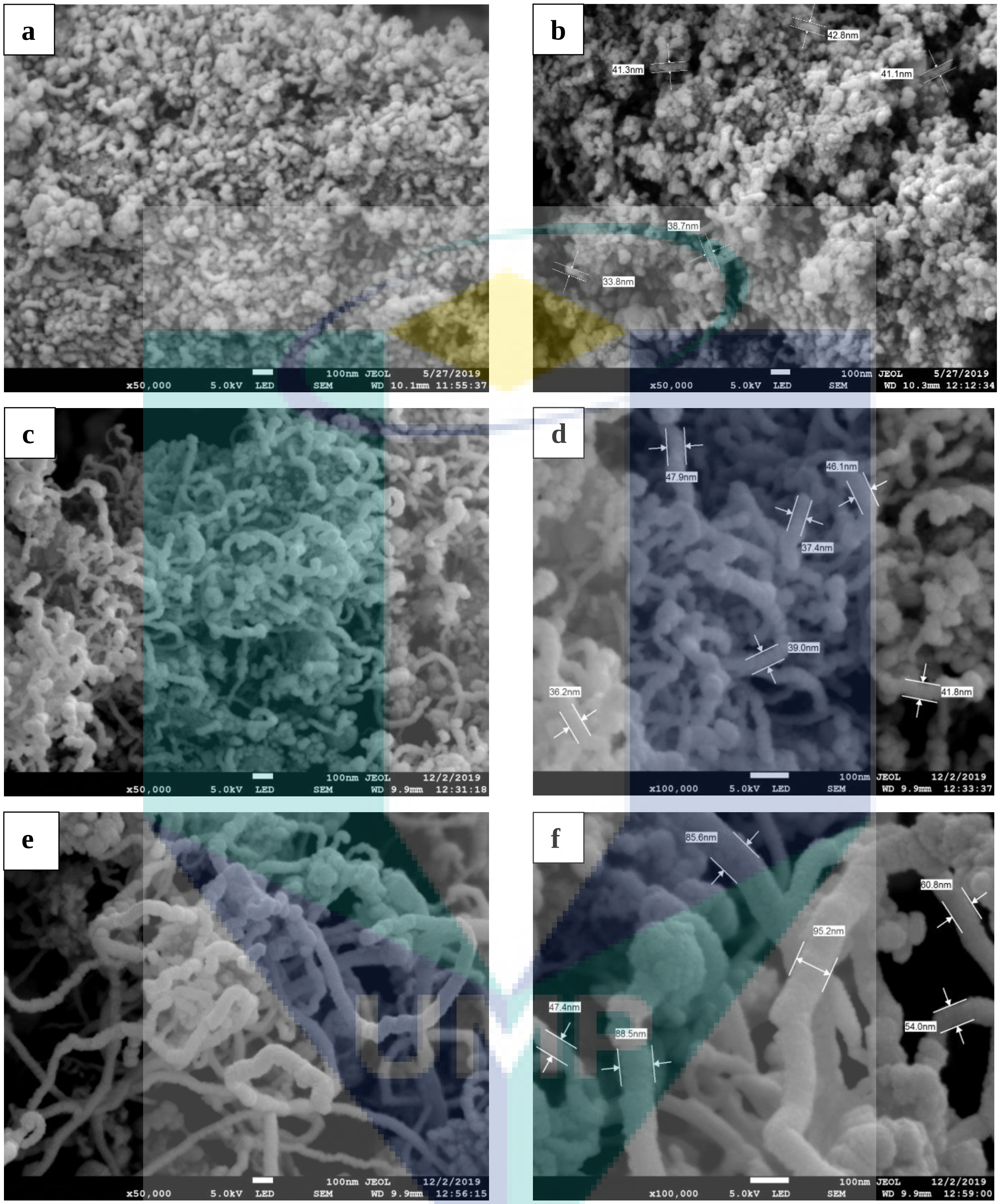

**Figure 3.8** FESEM micrographs of spent Ni–POFA catalysts at different Ni loadings; a-b) 10 wt% , c-d) 15 wt% and e-f) 20 wt% of Ni under 50,000× and 100,000× magnification, respectively

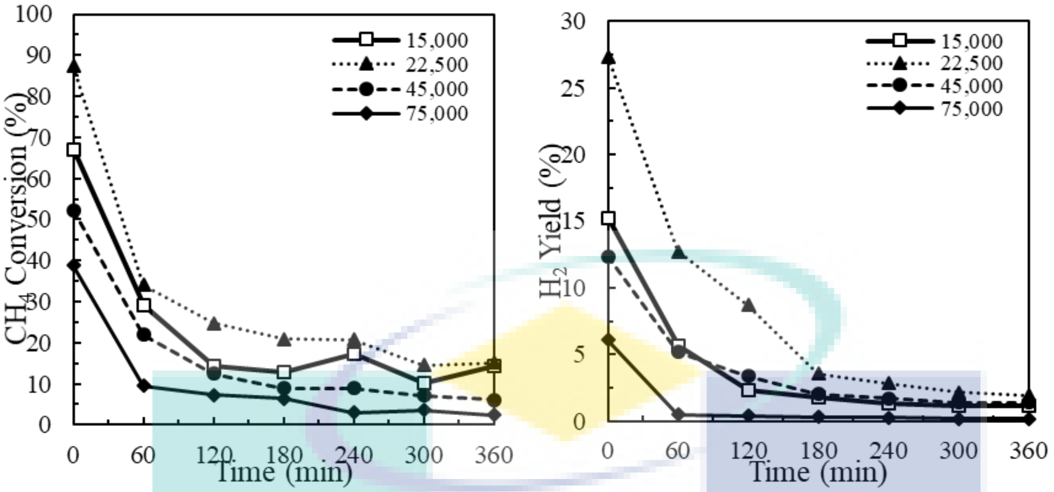

**Figure 3.9** a) $CH_4$ conversion and b) $H_2$ yield of Ni–POFA catalyst for the effect of GHSV (15,000, 22,500, 45,000 and 75,000) in methane cracking at 550 °C.

## 4. CONCLUSION

In summary, the pre-treatment of palm oil fuel ash (POFA) with citric acid solution using ultra-sonication technique has been selected as the best pre-treatment method. The pre-treatment has successfully improved the $SiO_2$ content from 42.4 to 72.0% from the removal of impurities in the POFA. The current work suggested that the pre-treatment of POFA has successfully improved the amount and crystallinity of $SiO_2$, increased the BET surface area and removed the impurities available in the POFA. Catalyst preparation method and Ni loading have significantly influenced the morphology of the catalyst thus the catalytic performance. Type of carbon formed on the spent Ni–POFA catalysts was also varied due to catalyst preparation method. In situ glycine-nitrate combustion employed for the synthesis of Ni–POFA catalyst gave high dispersion of Ni metal particles and exhibited an active catalytic activity in methane cracking. The Ni–POFA catalyst synthesized using in situ glycine-nitrate combustion method with 15 wt.% of Ni loading has exhibited the best performance in methane cracking reaction at 550°C. At the optimum GHSV of 22,500 mL/g.h, 15 wt.% Ni–POFA catalyst was an active catalyst the highest initial $CH_4$ conversion and $H_2$ yield of 87.0% of and 27.0%, respectively. In overall, all three objectives of the project have been complied and the work has successfully produced Ni catalyst supported on palm oil fuel ash (Ni–POFA) with a decent stability and catalytic activity for methane cracking process.

## ACHIEVEMENT

i) Name of articles/ manuscripts/ books published
  a) Book chapter: A Short Review on Production of Syngas via Glycerol Dry Reforming, *Conversion of Carbon Dioxide into Hydrocarbons Vol. 2 Technology*, *Environmental Chemistry for a Sustainable World* 41, 185-197 (2020)
  b) Article: A review on glycerol reforming processes over Ni-based catalyst for hydrogen and syngas productions, *International Journal of Hydrogen Energy,* (2019) https://doi.org/10.1016/j.ijhydene.2019.08.211
  c) Ni–supported palm oil fuel ash catalyst (Ni–POFA) from in situ glycine nitrate combustion for methane cracking *IOP Conference Series.: Material Science Engineering* 736 04210 (2020) https://doi.org/10.1088/1757-899X/736/4/042010

ii) Title of Paper presentations (international/ local)
N.A

iii) Human Capital Development
  a) Student: Nurul Husna Elyana binti Hanifa
     ID: MKC18010 (Master by Research)
  b) Student: Ali Saleh Mahmood
     ID: KKE 17012 (Master by Coursework)
  c) Student: Nur Zulhusni Binti Zulkifli
     ID: KA15225 (Undergraduate)
  d) Student: Nurul Ain Najihah Binti Abu Bakar
     ID: KA15134 (Undergraduate)

iv) Awards/ Others
N.A

v) Others
N.A

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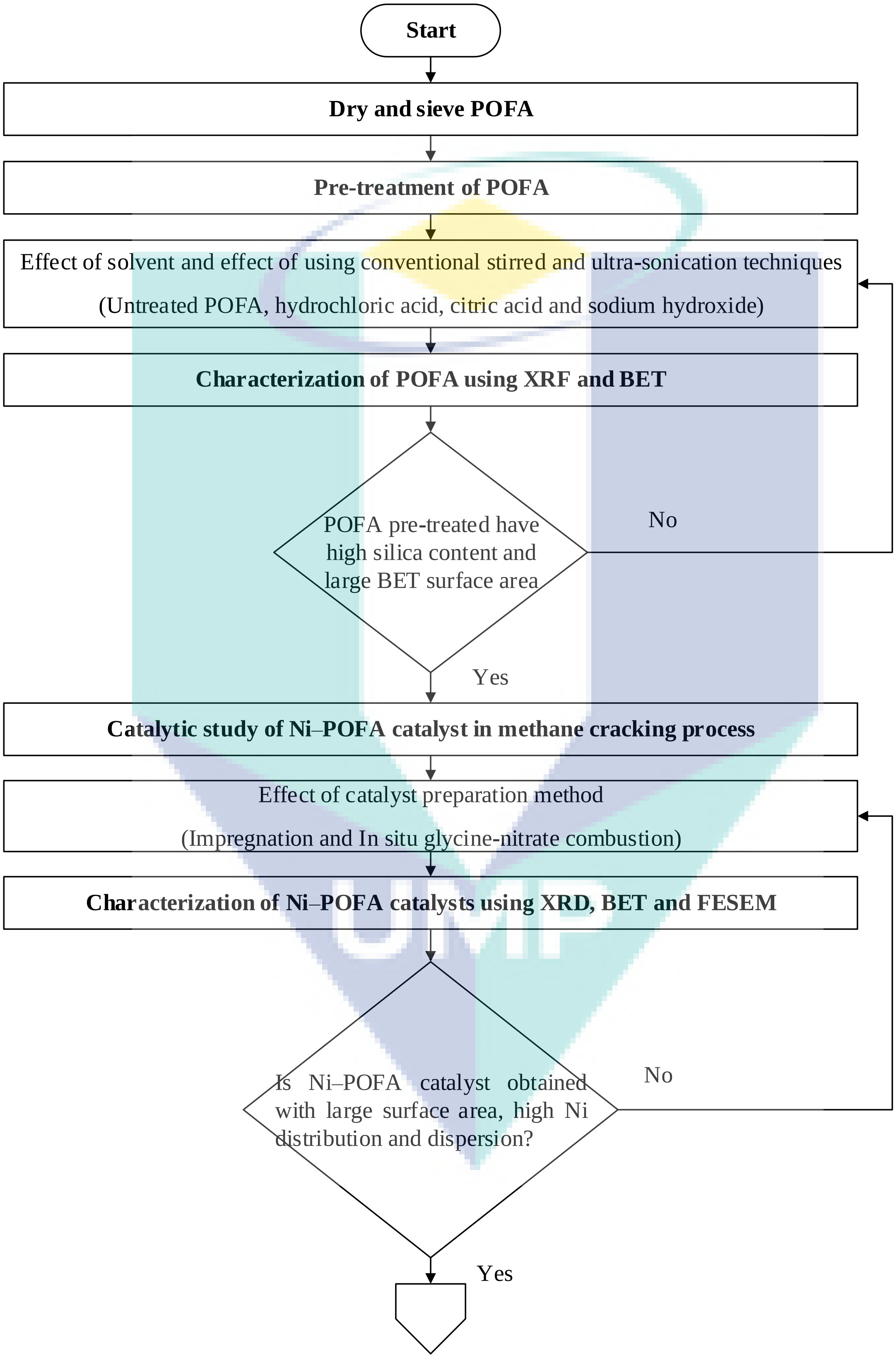
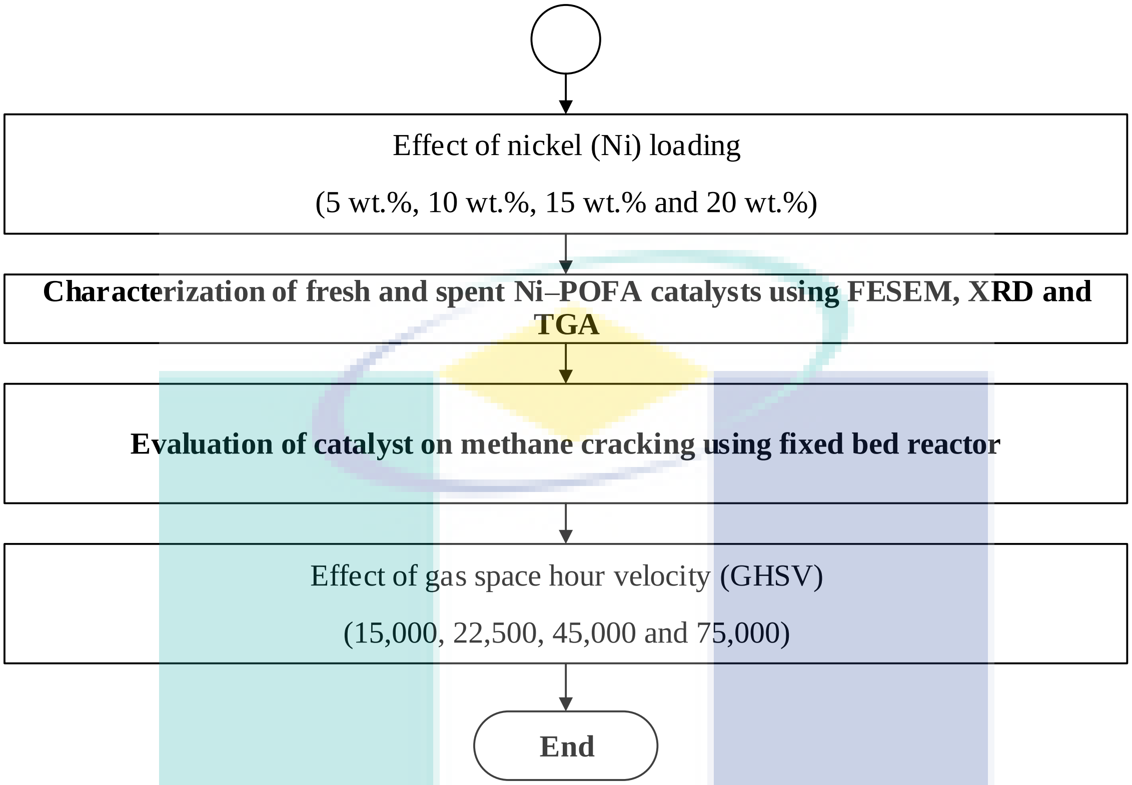
## APPENDIXES


Start
Dry and sieve POFA
Pre-treatment of POFA
Effect of solvent and effect of using conventional stirred and ultra-sonication techniques
(Untreated POFA, hydrochloric acid, citric acid and sodium hydroxide)
Characterization of POFA using XRF and BET
POFA pre-treated have high silica content and large BET surface area
No
Yes
Catalytic study of Ni–POFA catalyst in methane cracking process
Effect of catalyst preparation method
(Impregnation and In situ glycine-nitrate combustion)
Characterization of Ni–POFA catalysts using XRD, BET and FESEM
Is Ni–POFA catalyst obtained with large surface area, high Ni distribution and dispersion?
No
Yes



**Appendix A:** Overall workflow of the experimental works for this project