BIOGAS DRY REFORMING USING NICKEL SUPPORTED ON REGENERATED SPENT BLEACHING EARTH

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ABSTRACT

Currently, spent bleaching earth (SBE) is an abundant solid waste generated from crude palm oil refining that is discharged into landfills in Malaysia. It comprises a high percentage of silicon oxide (55-80 wt.%) and aluminium oxide (5-20 wt.%) with the potential to be reused as catalyst support. This study aims to evaluate the potential of nickel supported on regenerated spent bleaching earth (RSBE) for dry reforming of biogas into syngas. The RSBE was treated with different concentrations of nitric acid (x = 0.25M, 0.5M, 0.75M, and 1.0M), and then doped with 10 wt.% nickel using the wet-impregnation method. Subsequently, the synthesized catalysts were characterized to determine their reducibility, acidity, crystallinity, and the total surface area. The increase in acid concentration during RSBE treatment reduced the total surface area, acidity, and strength of the metal-support interaction of the Ni-RSBE catalysts. However, the high surface area, acidity and strong metal-support interaction of catalysts are beneficial to dry methane reforming in terms of anti-deactivation and catalytic activity. The performance of the catalysts was evaluated using a micro fixed bed reactor at 800 °C, 0.2 g of catalyst, and CH_4/CO_2 ratio of 1.2 at atmospheric pressure. The 10 wt.% Ni-RSBE catalyst with 0.25M and 0.5 M of acid treatment had almost similar catalytic performance to that without acid treatment. The conversion of CH_4 and CO_2 achieved was 55 to 57%, and 40 to 44%, respectively. Therefore, the Ni-RSBE catalyst without acid treatment was selected to further study the effect of nickel loading, reaction temperature, and CH_4/CO_2 ratio on the dry reforming of methane. Results showed that the presence of nickel promotes the dry reforming of methane as evident from the methane conversion, which increased from 15 to 56% with nickel loading from 0 to 15%. Besides, CH_4 and CO_2 conversion and syngas yield increased reaction temperature between 700 °C to 850 °C. In the aspect of the biogas feed ratio, the CH_4 conversion and H_2 yield decreased with the increase in the biogas feed ratio (0.7 - 1.5).

ABSTRAK

Pada masa ini, peluntur bumi terpakai (SBE) adalah sisa pepejal yang banyak terjana daripada penapisan minyak kelapa sawit mentah yang dilupuskan di tapak pelupusan di Malaysia. Ia mengandungi peratusan tinggi silikon oksida (55-80 berat%) dan aluminium oksida (5-20 berat%), dengan potensi untuk diguna semula sebagai penyokong mangkin. Kajian ini bertujuan untuk menilai potensi nikel di sokong oleh peluntur bumi terpakai yang dijana semula (RSBE) bagi pembentukan semula kering biogas kepada gas sintesis. RSBE dirawat dengan kepekatan asid nitrik berbeza (x = 0.25M, 0.5M, 0.75M dan 1.0M), dan kemudian didop dengan 10% berat nikel melalui kaedah impregnasi-basah. Mangkin-mangkin yang telah disintesis kemudian dicirikan bagi menentukan sifat pengurangan, keasidan, kehabluran dan jumlah luas permukaan. Tambahan kepekatan asid semasa rawatan RSBE mengurangkan jumlah luas permukaan, keasidan dan kekuatan interaksi logam-penyokong mangkin Ni-RSBE. Walau bagaimanapun, luas permukaan yang tinggi, keasidan dan kekuatan interaksi logam-penyokong mangkin adalah bermanfaat bagi pembentukan semula kering metana daripada segi anti penyahaktifan dan aktiviti bermangkin. Prestasi mangkin-mangkin ini dinilai menggunakan reaktor mikro lapisan tetap pada suhu 800 °C, mangkin 0.2 g dan CH_4/CO_2 berkadaran 1.2 pada tekanan atmosfera. Mangkin Ni-RSBE berat 10% dengan rawatan asid 0.25 dan 0.5 M mempunyai prestasi bermangkin yang hampir sama dengan tanpa rawatan asid. Penukaran CH_4 dan CO_2 dicapai dalam julat masing-masing adalah 55 ke 57% dan 40 ke 44%. Oleh yang demikian, mangkin Ni-RSBE tanpa rawatan asid telah dipilih bagi kajian seterusnya kesan muatan nikel, suhu tindak balas dan nisbah CH_4/CO_2 bagi pembentukan semula kering metana. Keputusan menunjukkan kehadiran nikel adalah menggalakkan pembentukan semula kering metana seperti dibuktikan daripada penukaran metana, dimana kenaikan daripada 15 ke 56% dengan muatan nikel bertambah daripada 0 ke 15%. Selain itu, penukaran CH_4 dan CO_2 serta hasil gas sintetik bertambah dengan kenaikan suhu tindak balas dalam julat kajian antara 700 hingga 850 ^{0}C. Dalam aspek nisbah suapan biogas, penukaran CH_4 dan hasil H_2 berkurangan dengan kenaikan nisbah suapan biogas (0.7-1.5).

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LIST OF ABBREVIATIONS

a.u.	-	Abstract Unit
AD	-	Anaerobic digestion
ATR	-	Auto thermal reforming
BE	-	Bleaching earth
BET-N_2	-	Brunauer Emmet Teller - Nitrogen
BHJ	-	Bulk Heterojunction
C_2H_4	-	Ethene
C_2H_6	-	Ethane
CH_4	-	Methane
CO	-	Carbon Monoxide
CPKO	-	Crude Palm Kernel Oil
CPO	-	Crude Palm Oil
CPR	-	Catalyst to Plastic Ratio
DMR	-	Dry Methane Reforming
DOR	-	Dry Oxidation Reforming
DR	-	Dry Reforming
EFB	-	Empty Fruit Bunches
EQA	-	Environment Quality Acts
EU	-	European Union
FFA	-	Free Fatty Acid
FFB	-	Fresh Fruit Bunches
GC	-	Gas Chromatography
GHG	-	Greenhouse Gases
GHSV	-	Gas Hourly Space Velocity
H_2	-	Hydrogen
HNO_3	-	Nitric Acid
LDPE	-	Low Density Polyethylene
M	-	Molarity
MFC	-	Mass Flow Controller
MPOB	-	Malaysian Palm Oil Board

M_w	-	Molecular Weight
N_2	-	Nitrogen
$Ni(NO_3)_2.6H_2O$	-	Nickel (II) Nitrate Hexahydrate
Ni-Al	-	Nickel Alumina
NiO	-	Nickel (II) Oxide
OD	-	Outside Diameter
PET	-	Polyethylene Terephthalate
POME	-	Palm Oil Mill Effluent
POR	-	Partial Oxidation Reforming
RBD	-	Refined Bleached Deodorized
RPM	-	Revolution per Minute
RSBE	-	Regenerated Spent Bleaching Earth
SBE	-	Spent Bleaching Earth
SCCM	-	Standard Cubic Centimetres per Minute
SiC	-	Silicon Carbide
SR	-	Steam Reforming
TGA	-	Thermo-Gravimetric Analysis
TPD	-	Temperature Program Desorption
TPR-H_2	-	Temperature Program Reduction - Hydrogen
XRD	-	X-Ray Diffraction
XRF	-	X-Ray Fluorescence

LIST OF SYMBOLS

^0C	-	Degree Celsius
2ɗ	-	Two Theta
P/P_0	-	Relative Pressure
ɓ	-	Beta
θ	-	Theta
ɚ	-	Gamma

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Biogas is a green and renewable source of energy generated by the biological breakdown of organic matter in the absence of oxygen (O_2), through the process of anaerobic digestion. Biogas is produced in landfills, municipal solid wastes, and palm oil mills. Typically, biogas mainly consists of 55-70% combustible methane (CH_4) and 30-45% non-combustible carbon dioxide (CO_2). In addition, biogas contains small amounts of hydrogen sulphide (H_2S), water vapour (H_2O), and other impurities (Chin *et al.*, 2013; Hosseini and Wahid, 2014). In Malaysia, biogas is mostly generated from palm oil mill effluent (POME) in the various palm oil mills currently operating in the country (Chin *et al.*, 2013; Kumaran *et al.*, 2016). It is now estimated that 58 million tons of POME is generated annually. As a result, the annual biogas potential from POME in Malaysia is approximately 15 billion cubic meters (m^3) (Ozturk *et al.*, 2017).

Despite its potential, biogas fractions such as CO_2 and CH_4 are considered the major greenhouse gases (GHG) that contribute to global warming and climate change (Chin *et al.*, 2013). In addition, GHG is detrimental to health, safety, and the environment along with significant implications on the livelihood and security of humanity (McMichael and Bennett, 2016; Khan *et al.*, 2018). Studies have revealed that mean global temperatures have risen by almost 1 °C since the start of the Industrial Revolution (the 1750s) (Steffen *et al.*, 2011; Abram *et al.*, 2016). As a result, governments and scientists worldwide have agreed that rising temperatures due to global warming must remain under 2 °C to avoid catastrophic climate change (COP21, 2015). Furthermore, numerous studies have been conducted worldwide to valorise CH_4 into liquid fuels or higher hydrocarbons such as methanol, formaldehyde, and propanol (Wood *et al.*, 2012; Ge *et al.*, 2014; Baltrusaitis and Luyben, 2015; Gür, 2016). However, these processes have either resulted in low yields or are unfeasible on an industrial-scale (Li *et al.*, 2011). Similarly, some studies have explored reaction pathways to convert other GHGs such as CO_2 into useful and environmental-friendly products such as syngas (Wood *et al.*, 2012; Mette *et al.*, 2014; Namwong *et al.*, 2016; Qin *et al.*, 2018).

Over time, the process of dry reforming (DR) has attracted considerable attention as it utilises the two greenhouse gases (GHG) as feedstock for synthesis gas (syngas) production. Syngas is a highly valuable product gas that consists of hydrogen (H_2) and carbon monoxide (CO) (Mette *et al.*, 2014). The DR process is favourable because it converts methane (CH_4) and carbon dioxide (CO_2) into syngas with H_2/CO ratios close to unity, which applies to Fischer-Tropsch synthesis (Ayodele *et al.*, 2016; Atashi *et al.*, 2017). In addition, DR is a highly endothermic reaction that occurs at favourable reaction temperatures from 600 °C to 800 °C (Mette *et al.*, 2016; Abdullah *et al.*, 2017). Syngas is a valuable gas mixture because it can act as a combustion promoter and feedstock for the production of liquid fuels and intermediate chemicals (Ayodele *et al.*, 2016; Zhang *et al.*, 2018).

Most research studies on DR aim to develop the most economical and effective catalyst to increase the selectivity, yield, and the timely production of hydrogen or syngas. The use of catalysts in DR is to increase the yield of product gases by lowering the activation energy (Li *et al.*, 2017). Nickel-based catalysts are considered promising alternative catalysts due to their low cost and relatively high catalytic activity compared to noble metals such as gold, platinum, and palladium (Basu, 2013; Wang *et al.*, 2018). However, the nickel-based catalysts have a higher tendency to form coke compared to the noble metal-based catalysts (Zhao *et al.*, 2016; Das *et al.*, 2018). Therefore, various metal oxides such as alumina are used as support for nickel catalysts to prevent or minimise sintering and coke formation (Jin *et al.*, 2018; Shen *et al.*, 2019). In addition, the catalyst support provides a larger surface area and metal dispersion that enhances the catalyst activity (Li *et al.*, 2018).

Physical refining is one of the most common practices in the downstream process of crude palm oil (CPO) refineries in Malaysia. The refining process of CPO consists of three primary operations; degumming, bleaching, and deodorisation. The method has several advantages including; high efficiency and high recovery at low operating costs due to fewer effluents generated (Ahmad *et al.*, 2018). The bleaching process uses a type of clay called bleaching earth or fuller earth (Ribeiro *et al.*, 2018). Bleaching earth improves the stability of the final product by adsorbing colouring matter and removing impurities such as soaps, phospholipids, oxidation products, trace metals and contaminants from CPO (Mat *et al.*, 2011; Loh *et al.*, 2013). The final residue from the bleaching earth's physical refining process is called spent bleaching earth (SBE) (Ribeiro *et al.*, 2018; Ahmad *et al.*, 2018).

The estimated quantity of bleaching earth used is approximately 0.8% of the CPO production capacity (Loh *et al.*, 2007). According to the Malaysian Palm Oil Board (MPOB) statistics, CPO production in Malaysia for the year 2017 was nearly 20 million tons, which eventually generating 160,000 tons of SBE. The SBE residues generated from the refining process contain around 30-40% oil by weight depending on the activity and processing conditions of the bleaching earth (Loh *et al.*, 2013). SBE is categorized as scheduled waste under the Environmental Quality Acts 1974 (EQA 1974), which is typically disposed-off in landfills. The oil content is generally retained without any further treatment due to the diverse composition of SBE. Due to increased environmental consciousness and the need for better solid waste management, many studies and researches have explored the reuse of SBE for various applications.

1.2 Problem Statement

Over the years, numerous researchers in the industry and academia have explored sustainable methods to recover oil and reactivate mineral-rich SBE. These processes are crucial to reducing environmental pollution and enhancing the economic interests of CPO refineries. Generally, clay consists of mainly silica and alumina, which is a typical catalyst support for the reforming process in the petrochemical industry. SBE which comprises a high percentage of silicon oxide (55-80 wt.%) and aluminium oxide (5-20 wt.%), has the potential to be reused as catalyst support for nickel catalysts. This approach could potentially minimise coke formation and increase the conversion of biogas and syngas yield.

In Malaysia, the POME generated from palm oil mills could potentially generate billions of cubic meters (m^3) of biogas annually. The National Key Economic Areas (NKEA) report of 2009 indicates that the POME generated was 57.42 million m^3, which could potentially generate grossly 1,607.76 million m^3 of biogas (NKEA, 2011). The composition of biogas consists of CH_4 and CO_2 ranging from 55% to 70% and 30% to 45 % by volume, respectively. Consequently, the biogas generated could be converted into syngas through the dry reforming (DR) process. This is a promising chemical process that requires further development due to its potential benefits to biogas valorisation efforts, global GHG reduction, and environmental sustainability of the crude palm oil industry. Many previous researchers had studied the most favourable conditions for biogas conversion, use of different catalysts, and modification of catalyst to obtain optimum yield. However, there are currently limited studies on the SBE-enhanced dry reforming of POME-based biogas in the literature.

Most research studies on DR aim to develop the most economical and effective catalyst to increase the selectivity, yield, and the timely production of hydrogen or syngas by lowering the activation energy (Li et al., 2017). Nickel-based catalysts are considered promising alternative catalysts due to their low cost and relatively high catalytic activity compared to noble metal catalysts (Basu, 2013; Wang et al., 2018). However, the Ni-based catalysts have a higher tendency to form coke compared to the noble metal-based catalysts (Zhao et al., 2016; Das et al., 2018). Therefore, various catalyst supports such as alumina and other metal oxides are used to prevent or minimise sintering and coke formation of Ni-based catalysts (Jin et al., 2018; Shen et al., 2019). Typically, the catalyst supports provide a larger surface area and metal dispersion that enhance the activity of catalysts (Li et al., 2018). Furthermore, various studies have demonstrated that the use of nitric acid (HNO_3) pre-treatment removes impurities, enhances metal catalyst dispersion, and catalyst activity (Li et al., 2005; Abbaslou et al., 2009; Li et al., 2015). Other studies have demonstrated that acid pre-treatment enhances the surface area and pore volume, which significantly improves the activity and mechanical stability of catalysts (Li et al., 2016; Wu et al., 2017).

Based on the preceding, it is envisaged that the nitric acid pre-treated high silica and alumina content SBE (Wambu et al., 2011) supported Ni catalysts will be a useful catalyst for the dry reforming (DR) of biogas. Therefore, this research seeks to investigate the utilisation of regenerated SBE as nickel catalyst support in the DR of biogas into valuable product gases. The results of this study will maximise the conversion of GHG into useful syngas by utilising SBE as catalyst support for nickel. The long-term goal is to mitigate environmental pollution through the valorisation of oil palm wastes into value-added products.

1.3 Objectives of the Study

The primary purpose of this study is to evaluate the prospects of regenerated spent bleaching earth (RSBE) as catalyst support in the biogas dry reforming. The specific objectives include the following:

1. To synthesize and characterize nickel (Ni) catalyst supported on the RSBE with different concentrations of nitric acid treatments.
2. To investigate the catalytic activities through the dry reforming of simulated biogas into syngas using a micro fixed bed reactor.
3. To evaluate the catalyst performance based on the effect of nickel loading on the RSBE, reaction temperatures, and CH_4/CO_2 feeding ratios.

1.4 Scope of the Study

The scope of the study was limited to the following activities, namely:

1. Pre-treatment to reactivate the clay materials in SBE before utilisation as catalyst support. These activities included the following:
   a. High-temperature calcination of the SBE at 800 °C to remove the residual oil and impurities.
   b. Preparation of six (6) catalysts consisting of 10 wt.% Ni supported on the untreated and treated SBE with acid at different nitric acid concentrations. In addition, a common catalyst of 10 wt.% Ni-ɔAl_2O_3 was also prepared and used for comparison.
   c. Characterization of catalyst properties by BET-N_2 for total surface area and pore size, XRD for crystallinity, TPR-H_2 for nickel reducibility, TPD-pyridine for catalyst acidity, and XRF for elemental composition and TGA for thermal stability.

2. Catalysts screening through dry reforming of simulated biogas in a fixed bed reactor with the following activities:
   a. The catalysts were tested at 800 °C, 0.2 g, simulated biogas 60 vol.% of CH_4 and 40 vol.% of CO_2 (typical sweet biogas composition) making a total flow of 100 SCCM for 5 hours of reaction time.
   b. Catalyst evaluation for the conversion of CH_4 and CO_2, and product gas yield of H_2/CO.

3. Based on the gas conversion and coke formation, the most promising catalyst was selected from objective 2 for further tests, which included:
   a. Evaluation of the catalyst performance by varying the temperature from 700 °C to 850 °C, nickel loading of 0 to 15 wt.% and CH_4/CO_2 feeding ratio of 0.7 to 1.5.

1.5 Significance of the Study

The review of the literature and preliminary findings indicate there is no study on the utilisation of RSBE as catalyst support for biogas dry reforming into syngas. Hence, the results and analysis of the catalyst characterisations will provide a basis for further research and development projects in catalytic synthesis. In addition, this study will provide novel insights required to address the growing environmental concerns about the utilisation of solid waste SBE along with the mitigation of CH_4, CO_2 and other GHGs based on dry reforming. Finally, this research will provide a theoretical and empirical basis for future research.

1.6 Outline of the Thesis

Chapter one of this research work presented the background of the study, problem statement along with the objectives, scopes, and significance of the study. Chapter two will present the review of the literature on the palm oil milling, crude palm oil refining process, POME, biogas, SBE and the background on Ni-based catalysts. Lastly, it will also present literature on the dry reforming process for syngas production. Chapter three will summarise the materials, methods, and equipment used to carry out the research work in this study. The results and discussions on the experimental studies and tests in the research work will be presented in chapter four. Lastly, chapter five will highlight the significant findings of the research work and offer recommendations for future research work.

REFERENCES

Abd Majid, R. & Mat, C. R. C. (2017). Regenerated Spent Bleaching Earth For The Decolourisation And BOD Reduction Of Palm Oil Mill Effluent. *Journal Of Oil Palm Research,* 29**,** 579-587.

Abdullah, B., Ghani, N. a. A. and Vo, D.-V. N. (2017). Recent Advances in Dry Reforming of Methane over Ni-Based Catalysts. *Journal of Cleaner Production,* 162**,** 170-185.

Abdullah, N., & Sulaiman, F. (2013). The oil palm wastes in Malaysia. Biomass Now ï Sustainable Growth and Use, 75ï 100.

Abram, N. J., Mcgregor, H. V., Tierney, J. E., Evans, M. N., Mckay, N. P., Kaufman, D. S., Thirumalai, K., Martrat, B., Goosse, H. and Phipps, S. J. (2016). Early Onset of Industrial-Era Warming across the Oceans and Continents. *Nature,* 536(7617)**,** 411.

Ahmad, H., Mee, M. T. Y., Noor, A. M. and Yusoff, M. S. A. (2018). Thermal Stability Evaluation of Refined Bleached Deodorized Palm Oil (RBDPO) from Different Refining Parameters for Standard Crude Palm Oil. *International Journal of Food Engineering,* 4(1).

Aishat, A., Olalekan, S., Arinkoola, A., & Omolola, J. (2015). Effect of Activation on Clays and Carbonaceous Materials in Vegetable Oil Bleaching: State of Art Review. *British Journal of Applied Science & Technology*, 5(2), 130ï 141.

Al-Fatesh, A. S. A., & Fakeeha, A. H. (2012). Effects of calcination and activation temperature on dry reforming catalysts. *Journal of Saudi Chemical Society*.

Alang Mahat, S. (2012). The Palm Oil Industry From The Perspective of Sustainable Development: A Case Study of Malaysian Palm Oil Industry. Ritsumeikan Asia Pacific University Japan, (September), 14. Retrieved from http://r-cube.ritsumei.ac.jp/bitstream/10367/4738/1/51210600.pdf

Alves, H. J., Bley Junior, C., Niklevicz, R. R., Frigo, E. P., Frigo, M. S., & Coimbra-Araújo, C. H. (2013). Overview of hydrogen production technologies from biogas and the applications in fuel cells. *International Journal of Hydrogen Energy,* 38(13), 5215ï 5225.

Arpornpong, N., Charoensaeng, A., Khaodhiar, S. & Sabatini, D. A. (2018). Formulation Of Microemulsion-Based Washing Agent For Oil Recovery From Spent Bleaching Earth-Hydrophilic Lipophilic Deviation Concept. *Colloids And Surfaces A-Physicochemical And Engineering Aspects,* 541**,** 87-96.

Atashi, H., Gholizadeh, J., Tabrizi, F. F., Tayebi, J. and Mousavi, S. A. H. S. (2017). Thermodynamic Analysis of Carbon Dioxide Reforming of Methane to Syngas with Statistical Methods. *International Journal of Hydrogen Energy,* 42(8)**,** 5464-5471.

Ayodele, B. V., Hossain, S. S., Lam, S. S., Osazuwa, O. U., Khan, M. R. and Cheng, C. K. (2016). Syngas Production from CO_2 Reforming of Methane over Neodymium Sesquioxide Supported Cobalt Catalyst. *Journal of Natural Gas Science and Engineering,* 34**,** 873-885.

Ayodele, B. V., Khan, M. R. & Cheng, C. K. (2017). Greenhouse Gases Abatement By Catalytic Dry Reforming Of Methane To Syngas Over Samarium Oxide-Supported Cobalt Catalyst. *International Journal Of Environmental Science And Technology,* 14**,** 2769-2782.

Babaki, H., Salem, A., & Jafarizad, A. (2008). Kinetic model for the isothermal activation of bentonite by sulfuric acid. Materials Chemistry and Physics.

Baltrusaitis, J. and Luyben, W. L. (2015). Methane Conversion to Syngas for Gas-to-Liquids (GTL): Is Sustainable CO_2 Reuse Via Dry Methane Reforming (DMR) Cost Competitive with SMR and ATR Processes? *ACS Sustainable Chemistry & Engineering,* 3(9)**,** 2100-2111.

Basu, P. (2013). *Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory.* London, United Kingdom (UK), Academic Press (Elsevier).

Belhaine, A., Ghezzar, M. R., Abdelmalek, F., Tayebi, K., Ghomari, A. & Addou, A. 2016. Removal Of Methylene Blue Dye From Water By A Spent Bleaching Earth Biosorbent. *Water Science And Technology,* 74**,** 2534-2540.

Boey, P. L., Saleh, M. I., Sapawe, N., Ganesan, S., Maniam, G. P., & Ali, D. M. H. (2011). Pyrolysis of residual palm oil in spent bleaching clay by modified tubular furnace and analysis of the products by GC-MS. *Journal of Analytical and Applied Pyrolysis*.

Brooks, D. D., Berbesi, R., & Hodgson, A. S. (2014). Optimization of the Bleaching Process. (1), 1ï 9.

Chen, W., Fan, Z., Pan, X., & Bao, X. (2008). Effect of confinement in carbon nanotubes on the activity of Fischer-Tropsch iron catalyst. *Journal of the American Chemical Society*.

Chen, X. J., Jiang, J. G., Tian, S. C. & Li, K. M. (2015). Biogas Dry Reforming For Syngas Production: Catalytic Performance Of Nickel Supported On Waste-Derived Sio2. *Catalysis Science & Technology,* 5**,** 860-868.

Chin, M. J., Poh, P. E., Tey, B. T., Chan, E. S. and Chin, K. L. (2013). Biogas from Palm Oil Mill Effluent (Pome): Opportunities and Challenges from Malaysia's Perspective. *Renewable and Sustainable Energy Reviews,* 26**,** 717-726.

Chong, C. L. (2012). Measurement and Maintenance of Palm Oil Quality. In Palm Oil: Production, Processing, Characterization, and Uses.

Choo, S. Y., Radam, A., Hassan, A., & Shamsudin, M. N. (2018). Market structure of Malaysian palm oil refining industry. *Asian Academy of Management Journal*, 23(2), 125ï 141.

COP21. (2015). Adoption of the Paris Agreement: Draft Decision (COP21). Conference of the Parties Twenty-first session Paris, France, 2015 Paris, France. United Nations Framework Convention on Climate Change (UNFCC), 32.

Das, S., Ashok, J., Bian, Z., Dewangan, N., Wai, M., Du, Y., Borgna, A., Hidajat, K. and Kawi, S. (2018). Silicaï Ceria Sandwiched Ni Coreï Shell Catalyst for Low Temperature Dry Reforming of Biogas: Coke Resistance and Mechanistic Insights. *Applied Catalysis B: Environmental,* 230**,** 220-236.

De Caprariis, B., De Filippis, P., Palma, V., Petrullo, A., Ricca, A., Ruocco, C., & Scarsella, M. (2016). Rh, Ru and Pt ternary perovskites type oxides BaZr(1-x)MexO_3 for methane dry reforming. Applied Catalysis A: General, 517, 47ï 55.

Dunford, N. T. (2012). Advancements in Oil and Oilseed Processing. *In Food and Industrial Bioproducts and Bioprocessing*.

Effendi, A., Hellgardt, K., Zhang, Z. G., & Yoshida, T. (2005). Optimising H_2 production from model biogas via combined steam reforming and CO shift reactions. Fuel.

Fakeeha, A. H., Alfatish, A. S., Soliman, M. A., & Ibrahim, A. A. (2006). Effect of changing CH_4/CO_2 ratio on hydrogen production by dry reforming reaction. 16th World Hydrogen Energy Conference 2006, WHEC 2006.

Fatah, N., Jalil, A. and Triwahyono, S. (2018). Platinum and Molybdenum Oxide Supported on Mesostructured Silica Nanoparticles for n-Pentane and Cyclohexane Isomerization. *Journal of Energy and Safety Technology (JEST), 1*(1).

Fernandes, C., Catrinescu, C., Castilho, P., Russo, P. A., Carrott, M. R., & Breen, C. (2007). Catalytic conversion of limonene over acid activated Serra de Dentro (SD) bentonite. Applied Catalysis A: General.

Fogler, H. S. (2006). Elements of Reaction Engineering. In Bioprocess Engineering.

Furusawa, T., Saito, K., Kori, Y., Miura, Y., Sato, M. and Suzuki, N. (2013). Steam reforming of naphthalene/benzene with various types of Pt-and Ni-based catalysts for hydrogen production. *Fuel, 103*, 111-121.

Ge, X., Yang, L., Sheets, J. P., Yu, Z. and Li, Y. (2014). Biological Conversion of Methane to Liquid Fuels: Status and Opportunities. *Biotechnology advances,* 32(8)**,** 1460-1475.

Gibon, V., Ayala, J. V., Dijckmans, P., Maes, J., & de Greyt, W. D. (2009). Future prospects for palm oil refining and modifications. OCL - Oleagineux Corps Gras Lipides, 16(4), 193ï 200.

Gnanamani, M. K., Hamdeh, H. H., Jacobs, G., Qian, D., Liu, F., Hopps, S. D., Davis, B. H. (2016). Fischer-Tropsch synthesis: Effect of Cu, Mn and Zn addition on activity and product selectivity of cobalt ferrite. RSC Advances.

Gunstone, F. D. (2011). Vegetable Oils in Food Technology: Composition, Properties and Uses (2nd ed.).

Gür, T. M. (2016). Comprehensive Review of Methane Conversion in Solid Oxide Fuel Cells: Prospects for Efficient Electricity Generation from Natural Gas. *Progress in Energy and Combustion Science,* 54**,** 1-64.

Hart, M. P., & Brown, D. R. (2004). Surface acidities and catalytic activities of acid-activated clays. *Journal of Molecular Catalysis A: Chemical*.

Heo, D. H., Lee, R., Hwang, J. H. and Sohn, J. M. (2016). The effect of addition of Ca, K and Mn over Ni-based catalyst on steam reforming of toluene as model tar compound. *Catalysis Today, 265*, 95-102.

Hongmei, L. and Yide, X. (2006). H2-TPR Study on Mo/HZSM-5 Catalyst for CH_4 Dehydroaromatization. *Chinese Journal of Catalysis,* 27(4)**,** 319-323.

Hosseini, S. E. and Wahid, M. A. (2014). Development of Biogas Combustion in Combined Heat and Power Generation. *Renewable and Sustainable Energy Reviews,* 40**,** 868-875.

Hussin, F. (2013). Acid Activation of Bleaching Earth for Crude Palm Oil Treatment. University Malaya, Kuala Lumpur.

Hussin, F., Aroua, M. K., & Daud, W. M. A. W. (2011). Textural characteristics, surface chemistry and activation of bleaching earth: A review. *Chemical Engineering Journal*, 170(1), 90ï 106.

Jin, F., Sun, H., Wu, C., Ling, H., Jiang, Y., Williams, P. T. and Huang, J. (2018). Effect of Calcium Addition on Mg-Alox Supported Ni Catalysts for Hydrogen Production from Pyrolysis-Gasification of Biomass. *Catalysis Today,* 309**,** 2-10.

Khan, M. N., Khan, M. A., Khan, S. and Khan, M. M. (2018). Effect of Air Conditioning on Global Warming and Human Health. *Modern Age Environmental Problems and Their Remediation.* (pp. 83-94). Springer.

Kheang, L. S., Foon, C. S., May, C. Y. and Ngan, M. A. (2006). A Study of Residual Oils Recovered from Spent Bleaching Earth: Their Characteristics and Applications. *American Journal of Applied Sciences,* 3(10)**,** 2063-2067.

Kim, S., Chun, D., Rhim, Y., Lim, J., Kim, S., Choi, H., Lee, S. and Yoo, J. (2015). Catalytic reforming of toluene using a nickel ion-exchanged coal catalyst. *international journal of hydrogen energy, 40*(35), 11855-11862.

Knochen, M., & Morales, G. (2015). Edible fats and oils. In Handbook of Mineral Elements in Food.

Kohn, M. P. (2012). Catalytic Reforming of Biogas for Syngas Production. PhD Thesis. Columbia University.

Komadel, P., & Madejová, J. (2013). Acid activation of clay minerals. In Developments in Clay Science.

Kumaran, P., Hephzibah, D., Sivasankari, R., Saifuddin, N. and Shamsuddin, A. H. (2016). A Review on Industrial Scale Anaerobic Digestion Systems Deployment in Malaysia: Opportunities and Challenges. *Renewable and Sustainable Energy Reviews,* 56**,** 929-940.

Kuuluvainen, V., Maki-Arvela, P., Eranen, K., Holappa, A., Hemming, J., Osterholm, H., Toukoniitty, B. & Murzin, D. Y. (2015). Extraction Of Spent Bleaching Earth In The Production Of Renewable Diesel. *Chemical Engineering & Technology,* 38**,** 769-776.

Laosiripojana, N. and Assabumrungrat, S. (2005). Catalytic dry reforming of methane over high surface area ceria. *Applied Catalysis B: Environmental, 60*(1-2), 107-116.

Li, D., Nakagawa, Y. and Tomishige, K. (2011). Methane Reforming to Synthesis Gas over Ni Catalysts Modified with Noble Metals. *Applied Catalysis A: General,* 408(1-2)**,** 1-24.

Li, F., Shen, B., Tian, L., Li, G., & He, C. (2016). Enhancement of SCR activity and mechanical stability on cordierite supported V_2O_5-WO_3/TiO_2 catalyst by substrate acid pretreatment and addition of silica. Powder Technology, 297, 384ï 391.

Li, J., Ma, L., Li, X., Lu, C., & Liu, H. (2005). Effect of nitric acid pretreatment on the properties of activated carbon and supported palladium catalysts. Industrial and Engineering Chemistry Research.

Li, W., Nie, X., Jiang, X., Zhang, A., Ding, F., Liu, M., Liu, Z., Guo, X. and Song, C. (2018). ZrO_2 Support Imparts Superior Activity and Stability of Co Catalysts for Co2 Methanation. *Applied Catalysis B: Environmental,* 220**,** 397-408.

Li, X., Li, D., Tian, H., Zeng, L., Zhao, Z.-J. and Gong, J. (2017). Dry Reforming of Methane over Ni/La_2O_3 Nanorod Catalysts with Stabilized Ni Nanoparticles. *Applied Catalysis B: Environmental,* 202**,** 683-694.

Li, Z., Liu, R., Xu, Y., & Ma, X. (2015). Enhanced Fischer-Tropsch synthesis performance of iron-based catalysts supported on nitric acid treated N-doped CNTs. Applied Surface Science.

Liu, Y., Huang, J., & Wang, X. (2008). Adsorption isotherms for bleaching soybean oil with activated attapulgite. JAOCS, Journal of the American Oil ChemistsôSociety.

Loh S. K., Choo Y. M. & Ma A. N., 2007. (2007). Residual oil from spent bleaching earth (SBE) for biodiesel and biolubricant applications. MPOB Information Series. ISSN 1511-7871, 2ï 5.

Loh, S. K., Cheong, K. Y. & Salimon, J. (2017). Surface-Active Physicochemical Characteristics Of Spent Bleaching Earth On Soil-Plant Interaction And Water-Nutrient Uptake: A Review. *Applied Clay Science,* 140**,** 59-65.

Loh, S. K., Cheong, K. Y., Choo, Y. M. & Salimon, J. 2015. Formulation And Optimisation Of Spent Bleaching Earth-Based Bio Organic Fertiliser. *Journal Of Oil Palm Research,* 27**,** 57-66.

Loh, S. K., James, S., Ngatiman, M., Cheong, K. Y., Choo, Y. M. and Lim, W. S. (2013). Enhancement of Palm Oil Refinery Wasteï Spent Bleaching Earth (SBE) into Bio Organic Fertilizer and Their Effects on Crop Biomass Growth. *Industrial crops and products,* 49**,** 775-781.

Loh, S. K., Lai, M. E., Ngatiman, M., Lim, W. S., Choo, Y. M., Zhang, Z., & Salimon, J. (2013). Zero discharge treatment technology of palm oil mill effluent. Journal of Oil Palm Research, 25(DEC), 273ï 281.

Lovell, E. C., Scott, J., & Amal, R. (2015). Ni-SiO_2 catalysts for the carbon dioxide reforming of methane: Varying support properties by flame spray pyrolysis. Molecules.

Ma, Z. & Zaera, F. (2006). Heterogeneous Catalysis By Metals. *Encyclopedia Of Inorganic Chemistry.* John Wiley & Sons, Ltd.

Malakootian, M., Haghighifard, N. A. J., Moussavi, G. & Hossaini, H. (2016). Investigation Of Ammonium Ion Adsorption Onto Regenerated Spent Bleaching Earth: Parameters And Equilibrium Study. *Environmental Engineering And Management Journal,* 15**,** 773-782.

Malaysian Palm Oil Board. (2019). Oil Palm Planted Area 2018. Retrieved September 1, 2019, from http://bepi.mpob.gov.my/index.php/en/statistics/area/189-area-2018.html

Malaysian Palm Oil Board. (2019). Production 2018. Retrieved September 1, 2019, from http://bepi.mpob.gov.my/index.php/en/statistics/production/186-production-2018.html

Malaysian Palm Oil Council (2019). Palm Oil Overview. Retrieved July 15, 2019, from http://mpoc.org.my/malaysian-palm-oil-industry/
Malaysian Palm Oil Council (2019). Palm Oil Overview. Retrieved July 15, 2019, from http://mpoc.org.my/malaysian-palm-oil-industry/
Malaysia Productivity Corporation. (2014). Recommendations Report: Reducing Unnecessary Regulatory Burden on Business - Growing Oil Palm.

Mat, R., Ling, O. S., Johari, A. and Mohammed, M. (2011). In Situ Biodiesel Production from Residual Oil Recovered from Spent Bleaching Earth. *Bulletin of Chemical Reaction Engineering & Catalysis,* 6(1)**,** 53-57.

Mat, R., Othman, S. N., Johari, A., Hassim, M. H. & Sulaiman, W. R. W. (2015). Naoh Treated Spent Bleaching Earth. *Jurnal Teknologi,* 75**,** 115-118.

Mba, O. I., Dumont, M. J., & Ngadi, M. (2015). Palm oil: Processing, characterization and utilization in the food industry - A review. Food Bioscience, Vol. 10, pp. 26ï 41.

Mcmichael, A. J. and Bennett, C. M. (2016). Global Environmental Change and Human Health. *The Ashgate Research Companion to the Globalization of Health.* (pp. 119-138). Routledge.

Mette, K., Kühl, S., Düdder, H., Kähler, K., Tarasov, A., Muhler, M. and Behrens, M. (2014). Stable Performance of Ni Catalysts in the Dry Reforming of Methane at High Temperatures for the Efficient Conversion of CO_2 into Syngas. *ChemCatChem,* 6(1)**,** 100-104.

Mette, K., KüHl, S., Tarasov, A., Willinger, M. G., KröHnert, J., Wrabetz, S., Trunschke, A., Scherzer, M., Girgsdies, F. and DüDder, H. (2016). High-Temperature Stable Ni Nanoparticles for the Dry Reforming of Methane. *ACS Catalysis,* 6(10)**,** 7238-7248.

Moral, A., Reyero, I., Alfaro, C., Bimbela, F. & Gandia, L. M. (2018). Syngas Production By Means Of Biogas Catalytic Partial Oxidation And Dry Reforming Using Rh-Based Catalysts. *Catalysis Today,* 299**,** 280-288.

Musa, M. L., Mat, R. & Abdullah, T. A. T. (2018). Catalytic Conversion Of Residual Palm Oil In Spent Bleaching Earth (SBE) By HZSM-5 Zeolite Based-Catalysts. *Bulletin Of Chemical Reaction Engineering And Catalysis,* 13**,** 456-465.

Namwong, L., Authayanun, S., Saebea, D., Patcharavorachot, Y. and Arpornwichanop, A. (2016). Modeling and Optimization of Proton-Conducting Solid Oxide Electrolysis Cell: Conversion of Co2 into Value-Added Products. *Journal of Power Sources,* 331**,** 515-526.

NKEA. (2011). Biogas Capture and CDM Project Implementation for Palm Oil Mills. *National Key Economic Areas (NKEA). National Biogas Implementation (EPP 5)*.

Oil Palm Blog (2016) Oil Palm Knowledge Base: Physical Refining ï Bleaching. Retrieved August 15, 2019, from https://oilpalmblog.wordpress.com/2015/12/26/physical-refining-bleaching/

Okwara C. A. & Osoka E. C. (2006). Caustic Activation Of Local Clays for Palm Oil Bleaching. Journal of Engineering and Applied Sciences, 1(4), 526ï 529.

Ozturk, M., Saba, N., Altay, V., Iqbal, R., Hakeem, K. R., Jawaid, M. and Ibrahim, F. H. (2017). Biomass and Bioenergy: An Overview of the Development Potential in Turkey and Malaysia. *Renewable and Sustainable Energy Reviews,* 79**,** 1285-1302.

Pakhare, D., & Spivey, J. (2014). A review of dry (CO_2) reforming of methane over noble metal catalysts. Chemical Society Reviews.

Panda, A. K., Mishra, B. G., Mishra, D. K. and Singh, R. K. (2010). Effect of Sulphuric Acid Treatment on the Physico-Chemical Characteristics of Kaolin Clay. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 363(1-3)**,** 98-104.

Pizzuti, L., Martins, C. and Lacava, P. (2016). Laminar Burning Velocity and Flammability Limits in Biogas: A Literature Review. *Renewable and Sustainable Energy Reviews,* 62**,** 856-865.

Pure, I. U. O., Symbols, A. C. C. O. P.-C., Terminology & Whiffen, D. H. (1979). *Manual Of Symbols And Terminology For Physicochemical Quantities And Units*, Pergamon Press.

Qian, K. and Kumar, A. (2017). Catalytic reforming of toluene and naphthalene (Model tar) by char supported nickel catalyst. *Fuel, 187*, 128-136.

Qin, B., Li, Y., Fu, H., Wang, H., Chen, S., Liu, Z. and Peng, F. (2018). Electrochemical Reduction of CO_2 into Tunable Syngas Production by Regulating Crystal Facets of Earth-Abundant Zn Catalyst. *ACS applied materials & interfaces*.

Rao, P. V., Baral, S. S., Dey, R. and Mutnuri, S. (2010). Biogas Generation Potential by Anaerobic Digestion for Sustainable Energy Development in India. *Renewable and sustainable energy reviews,* 14(7)**,** 2086-2094.

Rapagná, S., Provendier, H., Petit, C., Kiennemann, A., & Foscolo, P. U. (2002). Development of catalysts suitable for hydrogen or syn-gas production from biomass gasification. Biomass and Bioenergy.

Ribeiro, J. A., Almeida, E. S., Neto, B. A., Abdelnur, P. V. and Monteiro, S. (2018). Identification of Carotenoid Isomers in Crude and Bleached Palm Oils by Mass Spectrometry. *LWT,* 89**,** 631-637.

Ross, J. R. H. 2012. *Heterogeneous Catalysis: Fundamentals And Applications*, Elsevier.

Rossi, M., Gianazza, M., Alamprese, C., & Stanga, F. (2003). The role of bleaching clays and synthetic silica in palm oil physical refining. Food Chemistry.

Saad, J. M. & Williams, P. T. (2016). Pyrolysis-Catalytic-Dry Reforming Of Waste Plastics And Mixed Waste Plastics For Syngas Production. *Energy & Fuels,* 30**,** 3198-3204.

Saad, J. M. & Williams, P. T. (2017). Pyrolysis-Catalytic Dry (CO_2) Reforming Of Waste Plastics For Syngas Production: Influence Of Process Parameters. *Fuel,* 193**,** 7-14.

Sabour, M. R. & Shahi, M. (2018). Spent Bleaching Earth Recovery Of Used Motor-Oil Refinery. *Civil Engineering Journal-Tehran,* 4**,** 572-584.

Sahafi, S. M., Goli, S. A. H., Tabatabaei, M., Nikbakht, A. M. & Pourvosoghi, N. (2016). The Reuse Of Waste Cooking Oil And Spent Bleaching Earth To Produce Biodiesel. *Energy Sources Part A-Recovery Utilization And Environmental Effects,* 38**,** 942-950.

Salahudeen, N., Ahmed, A. S., Ajinomoh, C. S., & Hamza, H. (2012). Surface Area Enhancement of Pindiga Bentonitic Clay for. Petroleum Technology Development Journal, 2(2), 1ï 11.

Salleh, N., Shamsudin, Z., Juoi, J. M. & Mustafa, Z. (2017). Effects Of Heating Rates And Sbe Loading On Sintered Properties Of Spent Bleach Earth/Recycled Glass Composite. *Journal Of Mechanical Engineering And Sciences,* 11**,** 3104-3115.

San-José-Alonso, D., Juan-Juan, J., Illán-Gómez, M. J., & Román-Martínez, M. C. (2009). Ni, Co and bimetallic Ni-Co catalysts for the dry reforming of methane. Applied Catalysis A: General, 371(1ï 2), 54ï 59.

Saputra, E., Saputra, R., Nugraha, M. W., Irianty, R. S. & Utama, P. S. (2018). Removal Of Methylene Blue From Aqueous Solution Using Spent Bleaching Earth. *In:* Evelyn (Ed.) *2nd International Conference On Oleo And Petrochemical Engineering.*

Sedghamiz, M., Raeissi, S., Attar, F., Salimi, M. & Mehrabi, K. (2019). In-Situ Transesterification Of Residual Vegetable Oil In Spent Bleaching Clay With Alkali Catalysts Using CCD-RSM Design Of Experiment. *Fuel,* 237**,** 515-521.

Shen, J., Reule, A. A. and Semagina, N. (2019). Ni/$MgAl_2O_4$ Catalyst for Low-Temperature Oxidative Dry Methane Reforming with CO_2. *International Journal of Hydrogen Energy*.

Silva, S. M., Sampaio, K. A., Ceriani, R., Verhé, R., Stevens, C., De Greyt, W., & Meirelles, A. J. A. (2014). Effect of type of bleaching earth on the final color of refined palm oil. LWT - Food Science and Technology.

Smoláková, L., Kout, M., Ļapek, L., Rodriguez-Gomez, A., Gonzalez-Delacruz, V. M., Hromádko, L., & Caballero, A. (2016). Nickel catalyst with outstanding activity in the DRM reaction prepared by high temperature calcination treatment. International Journal of Hydrogen Energy, 41(20), 8459ï 8469.

Steffen, W., Grinevald, J., Crutzen, P. and Mcneill, J. (2011). The Anthropocene: Conceptual and Historical Perspectives. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences,* 369(1938)**,** 842-867.

Sugiharto, R., Hidayati, S. & Cholik, R. (2019). Application Of Response Surface Methodology To Evaluate Biodiesel Production From Spent Bleaching Earth By In Situ Transesterification Process. *In:* Suhartini, S., Bekti, W. S., Abdullah, A. G., Ariesta, R. L., Rahmah, N. L., Perdani, C. G., Istianah, N., Septifani, R., Lusiana, N., Widyastuti, E., Silalahi, R. L. R., Iqbal, Z., Mustaqiman, A. N., Basyariah, M. A. K. & Ali, D. Y. (Eds.) *International Conference On Green Agro-Industry And Bioeconomy.*

Suryani, A., Mubarok, Z., Suprihatin, Romli, M., Yunira, E. N. & Iop (2017). Process Design Of In Situ Esterification-Transesterifica Tion For Biodiesel Production From Residual Oil Of Spent Bleaching Earth (Sbe). *International Conference On Biomass: Technology, Application, And Sustainable Development, 2016.*

Taiko Group (2019). Chemical Composition: Taiko Bleaching Earth. Retrieved Jan 10, 2019, from https://clay.taikogroup.net/product/

Tang, J., Mu, B., Wang, W. B., Zheng, M. S. & Wang, A. Q. (2016). Fabrication Of Manganese Dioxide/Carbon/Attapulgite Composites Derived From Spent Bleaching Earth For Adsorption Of Pb(Ii) And Brilliant Green. *Rsc Advances,* 6**,** 36534-36543.

Tang, J., Mu, B., Zheng, M. S. & Wang, A. Q. (2015). One-Step Calcination Of The Spent Bleaching Earth For The Efficient Removal Of Heavy Metal Ions. *Acs Sustainable Chemistry & Engineering,* 3**,** 1125-1135.

Tang, J., Mu, B., Zong, L. & Wang, A. Q. (2018). One-Step Synthesis Of Magnetic Attapulgite/Carbon Supported Nife-Ldhs By Hydrothermal Process Of Spent Bleaching Earth For Pollutants Removal. *Journal Of Cleaner Production,* 172**,** 673-685.

Tang, J., Mu, B., Zong, L., Zheng, M. S. & Wang, A. Q. (2015). Fabrication Of Attapulgite/Carbon Composites From Spent Bleaching Earth For The Efficient Adsorption Of Methylene Blue. *Rsc Advances,* 5**,** 38443-38451.

Tang, J., Mu, B., Zong, L., Zheng, M. S. & Wang, A. Q. (2017). Facile And Green Fabrication Of Magnetically Recyclable Carboxyl-Functionalized Attapulgite/Carbon Nanocomposites Derived From Spent Bleaching Earth For Wastewater Treatment. *Chemical Engineering Journal,* 322**,** 102-114.

Timofeeva, M. N., Panchenko, V. N., Krupskaya, V. V., Gil, A., & Vicente, M. A. (2017). Effect of nitric acid modification of montmorillonite clay on synthesis of solketal from glycerol and acetone. *Catalysis Communications*, *90*, 65ï 69.

Usman, M. A., Ekwueme, V. I., Alaje, T. O., & Mohammed, A. O. (2012). Characterization, Acid Activation, and Bleaching Performance of Ibeshe Clay, Lagos, Nigeria. ISRN Ceramics.

Usman, M., Wan Daud, W. M. A., & Abbas, H. F. (2015). Dry reforming of methane: Influence of process parametersð A review. Renewable and Sustainable Energy Reviews, 45, 710ï 744.

Valenzuela Díaz, F. R., & De Souza Santos, P. (2001). Studies on the acid activation of Brazilian smectitic clays. Quimica Nova.

Van Den Berg, R., Zeļ eviĺ , J., Sehested, J., Helveg, S., De Jongh, P. E., & De Jong, K. P. (2016). Impact of the synthesis route of supported copper catalysts on the performance in the methanol synthesis reaction. Catalysis Today, Vol. 272, pp. 87ï 93.

Wafti, N. S. A., Yoo, C. K., Lin, S. W., Yaw, T. C. S., & Abdullah, L. C. (2011). Regeneration and characterization of spent bleaching clay. Journal of Oil Palm Research, 23(April), 999ï 1004.

Wambu, E. W., Muthakia, G. K. and Shiundu, P. M. (2011). Kinetics and Thermodynamics of Aqueous Cu (II) Adsorption on Heat Regenerated Spent Bleaching Earth. *Bulletin of the Chemical Society of Ethiopia,* 25(2).

Wan, D. J., Wu, L. R., Liu, Y. D., Chen, J., Zhao, H. L. & Xiao, S. H. (2019). Enhanced Adsorption Of Aqueous Tetracycline Hydrochloride On Renewable Porous Clay-Carbon Adsorbent Derived From Spent Bleaching Earth Via Pyrolysis. *Langmuir,* 35**,** 3925-3936.

Wang, N., Chu, W., Zhang, T. & Zhao, X. S. (2012). Synthesis, Characterization And Catalytic Performances Of Ce-SBA-15 Supported Nickel Catalysts For Methane Dry Reforming To Hydrogen And Syngas. *International Journal Of Hydrogen Energy,* 37**,** 19-30.

Wang, N., Yu, X. P., Shen, K., Chu, W. & Qian, W. Z. (2013). Synthesis, Characterization And Catalytic Performance Of MgO-Coated Ni/SBA-15 Catalysts For Methane Dry Reforming To Syngas And Hydrogen. *International Journal Of Hydrogen Energy,* 38**,** 9718-9731.

Wang, S. and Lu, G. Q. (1998). Effects of Acidic Treatments on the Pore and Surface Properties of Ni Catalyst Supported on Activated Carbon. *Carbon,* 36(3)**,** 283-292.

Wang, Y., Yao, L., Wang, S., Mao, D. and Hu, C. (2018). Low-Temperature Catalytic CO_2 Dry Reforming of Methane on Ni-Based Catalysts: A Review. *Fuel Processing Technology,* 169**,** 199-206.

Wood, D. A., Nwaoha, C. and Towler, B. F. (2012). Gas-to-Liquids (GTL): A Review of an Industry Offering Several Routes for Monetizing Natural Gas. *Journal of Natural Gas Science and Engineering,* 9**,** 196-208.

Wu, D., Zhang, Y., & Li, Y. (2017). Mechanical stability of monolithic catalysts: Improving washcoat adhesion by FeCrAl alloy substrate treatment. *Journal of Industrial and Engineering Chemistry*, 56, 175ï 184.

Wu, Y. M., Yang, J., Fan, X. L., Fu, S. F., Sun, M. T., & Guo, R. B. (2017). Elimination of methane in exhaust gas from biogas upgrading process by immobilized methane-oxidizing bacteria. Bioresource Technology.

Yasyerli, S., Filizgok, S., Arbag, H., Yasyerli, N., & Dogu, G. (2011). Ru incorporated Ni-MCM-41 mesoporous catalysts for dry reforming of methane: Effects of Mg addition, feed composition and temperature. *International Journal of Hydrogen Energy*.

Zhang, P. L., Dong, S. T., Li, B. C., Wei, X. D. & Zhang, J. P. (2018). Durable And Fluorine-Free Superhydrophobic Coatings From Palygorskite-Rich Spent Bleaching Earth. *Applied Clay Science,* 157**,** 237-247.

Zhang, Y., Sahir, A. H., Tan, E. C., Talmadge, M. S., Davis, R., Biddy, M. J. and Tao, L. (2018). Economic and Environmental Potentials for Natural Gas to Enhance Biomass-to-Liquid Fuels Technologies. *Green Chemistry,* 20(23)**,** 5358-5373.

Zhao, X., Li, H., Zhang, J., Shi, L. and Zhang, D. (2016). Design and Synthesis of Nice@ M-Sio2 Yolk-Shell Framework Catalysts with Improved Coke and Sintering-Resistance in Dry Reforming of Methane. *International Journal of Hydrogen Energy,* 41(4)**,** 2447-2456.