CATALYTIC CRACKING OF RESIDUAL PALM OIL AND REGENERATION OF SPENT BLEACHING EARTH

MOHD LUKMAN BIN MUSA @ AB GHANI

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Chemical Engineering)

School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia

JULY 2019

DEDICATION

To my beloved parents, wife, kids and friends.

ACKNOWLEDGEMENT

All thanks to God for giving me the wisdom, strength, protection, guidance, patience and courage to successfully complete the PhD program in Universiti Teknologi Malaysia. I would like to thank my supervisors, PM Dr. Ramli Bin Mat and Dr. Tuan Amran Tuan Abdullah for their guidance and inspiration during the research. Your prompt attentions, motivations, assistance, encouragements and understanding are highly appreciated.

I wish to thank Mr Mohd Latfi bin Che Haron and Miss Zainab binti Salleh from the Analytical Laboratory in Faculty of Chemical Engineering, as well as Miss Ambiga from University Industry Research Lab (UIRL), the entire staff and students in Chemical Reaction Engineering Group (CREG) and Institute of Future Energy (IFE) for their technical assistance and all the helps given throughout my research in Universiti Teknologi Malaysia. I am also grateful to everyone in UTM whose names are too numerous to mention who were always there to ease my stress. Gratitude is also given to my research group members for many enlightening discussions and criticisms.

I am highly indebted to my parents whose blessings I believe have taking me this far in my academic life. I want to specially thank my family for their love, encouragement and support, together with their patience and endurance.

Finally, I wish to acknowledge the support from Ministry of Higher Education, Malaysia, as well as Universiti Teknologi Malaysia for the *Biasiswa Separuh Masa* scholarship and financial support given during my research.

ABSTRACT

Bleaching earth is used to remove colour, phospholipids, oxidized products, metals and residual gums in the palm oil process refinery. Once adsorption process ends, the spent bleaching earth (SBE) which contains approximately 20-40 wt. % of the adsorbed oil is usually disposed to landfills. This study was carried out to recover the residual palm oil and regenerate the SBE. The oil content in SBE was recovered by catalytic cracking method using transition metal (Cuprum, Zinc, Chromium and Nickel) doped HZSM-5. Transition metal was introduced in HZSM-5 zeolite using incipient wetness impregnation method. The physicochemical properties of the catalysts were characterized using X-ray diffraction, Fourier transform infrared, nitrogen adsorption and temperature programmed desorption of ammonia. Liquid products obtained from cracking were analyzed by gas chromatography-mass spectrometry. The Ni/HZSM-5 zeolite exhibited the highest yields of alkenes. The performance of Ni loaded (5 wt. %, 10 wt. %, 15wt. %) on HZSM-5 zeolite for cracking of residual oil in SBE then was investigated for further study. The 15 wt. % of Ni doped on HZSM-5 zeolite exhibited the highest yields of alkenes and alkanes. Response surface methodology was employed to study the relationships of catalytic cracking of residual palm oil in SBE such as temperature, heating time and nitrogen flow rate on liquid products yield over 15%Ni/HZSM-5 catalyst and the optimization of the process have been carried out. The optimum liquid products yield of catalytic cracking of residual palm oil in SBE was 12.91 wt. % and achieved at 452 ^{o}C, 160 min of heating time and 86 mL/min of nitrogen flow rate. The regeneration of SBE by pyrolysis at high temperature (500 ^{o}C) followed with sulphuric acid (H_2SO_4) solution treatment at different concentration (0.5-3.0 M) for the crude palm oil and methylene blue decolourisation was also investigated. The results showed that the regenerated SBE using 1.5 M H_2SO_4 was identified as an optimal concentration of H_2SO_4 treatment.

ABSTRAK

Tanah luntur digunakan untuk menyingkirkan warna, fosfolipid, produk teroksida, logam dan sisa perekat di dalam proses penapisan minyak kelapa sawit. Setiap kali proses penjerapan berakhir, sisa tanah luntur (SBE) yang mengandungi lebih kurang 20-40 wt. % minyak yang dijerap biasanya dibuang ke tapak pembuangan sampah. Kajian ini dijalankan untuk memperoleh kembali baki minyak kelapa sawit dan menjana semula SBE. Minyak yang terkandung dalam SBE telah diperoleh kembali menggunakan kaedah pemecahan bermangkin menggunakan logam peralihan (kuprum, zink, kromium and nikel) yang dimuatkan dalam HZSM-5. Logam peralihan yang diperkenalkan dalam zeolite HZSM-5 adalah menggunakan kaedah pengisitepuan basah. Sifat-sifat fisikokimia mangkin telah dicirikan menggunakan pembelauan sinar-X, inframerah transformasi Fourier, penjerapan nitrogen dan penyahjerapan berprogram suhu amonia. Produk cecair diperoleh daripada pemecahan ini telah dianalisa dengan spektrometri jisim kromatografi gas. Zeolite Ni/HZSM-5 menunjukkan hasil alkena yang paling tinggi. Prestasi Ni yang dimuatkan (5 wt. %, 10 wt. %, 15 wt. %) dalam zeolite HZSM-5 untuk pemecahan baki minyak dalam SBE kemudian disiasat untuk kajian lanjut. 15 wt. % Ni yang terdop dalam zeolite HZSM-5 menunjukkan hasil alkena dan alkana yang paling tinggi. Kaedah sambutan permukaan telah digunakan untuk mengkaji hubungan pemecahan bermangkin baki minyak kelapa sawit dalam SBE seperti suhu, masa pemanasan dan kadar alir nitrogen terhadap hasil produk cecair yang diperolehi daripada mangkin 15%Ni/HZSM-5 dan pengoptimuman proses telah disiasat. Hasil optimum produk cecair dari pemecahan bermangkin baki minyak kelapa sawit dalam SBE adalah 12.91 wt. % dan dicapai pada 452 ^{o}C, 160 min masa pemanasan dan 86 mL/min kadar alir nitrogen. Penjanaan semula SBE oleh pemecahan pada suhu tinggi (500 ^{o}C) diikuti dengan rawatan larutan asid sulfurik (H_2SO_4) pada kepekatan yang berlainan (0.5-3.0 M) untuk penyahwarnaan minyak mentah kelapa sawit dan metilena biru juga turut disiasat. Hasil keputusan menunjukkan bahawa penjanaan semula SBE menggunakan 1.5 M H_2SO_4 telah dikenalpasti sebagai kepekatan optimum rawatan H_2SO_4.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

SBE	-	Spent bleaching earth
Fe	-	Ferrum (Iron)
Cu	-	Cuprum (Copper)
Cr	-	Chromium
Zn	-	Zink
Ni	-	Nickel
Co	-	Cobalt
V	-	Vanadium
C	-	Carbon
CO	-	Carbon oxide
CO_2	-	Carbon dioxide
H_2O	-	Water
AlO_4	-	Aluminum oxide
H_2	-	Hidrogen
MAH	-	Monoaromatic hydrocarbon
PAH	-	Polycyclic aromatic
HCl	-	Hydrochloric acid
M	-	Molar
H_2SO_4	-	Suilphuric Acid
RSBE	-	Regenerated spent bleaching earth
MB	-	Methylene blue
TGA	-	Thermogravimetric Analysis
XRD	-	X-ray diffraction
FTIR	-	Fourier Transform Infra-Red
TPD-NH_3	-	Temperature programmed desorption of ammonia
GC-MS	-	Gas Chromatography-Mass Spectroscopy
CCD	-	Central composite design
RSM	-	Responds surface methodology
SEM	-	Scanning electron microscopy
BE	-	Bleaching earth

CPO	-	Crude Palm Oil
ABE	-	Activated bleaching earth
FAC	-	Fatty acids composition
FFA	-	Free fatty acids
PV	-	Peroxide value
SC-CO_2	-	Supercritical carbon dioxide
BOD	-	Biological oxygen demand
POME	-	Palm oil mill effluent
SV	-	Spatial velocity
KOH	-	Potassium Hydroxide
Atm	-	Atmosphere
MFI	-	Mordenite Framework Inverted
BTX	-	Benzene, Toluene, Xylene
BET	-	Brunauer-Emmet-Teller
BJH	-	Barrett-Joyner-Halenda
wt.	-	weight
ANOVA	-	Analysis of variace
DF	-	degree of freedom
SSR	-	Sum of squares regression,
SSE	-	Sum of squares errors,
DF_{SSR}	-	Degree of freedom for SSR
DF_{SSE}	-	Degree of freedom for SSE
(R)	-	Coefficient of correlation
UVO	-	Used vegetable oil
IUPAC	-	International union of Pure and applied chemistry classification
ASTM	-	American society for testing and materials

LIST OF SYMBOLS

Å - Angstrom
α - Alpha
θ - Theta
λ - Wavelength
kV - kilovolt

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

Vegetable oils have recently got attention due to their environmental benefits and renewable resources. They have the potential to substitute for the petroleum fuels in the near future (Demirbas, 2007). Currently, Malaysia is one of the largest producers of palm oil and exporter of palm oil. Therefore, there has been a sustained interest in the utilization of palm oil and palm oil biomass for the production of environmentally friendly biofuels (Chew and Bhatia, 2008). In addition, palm oil and palm oil biomass are the promising feedstock for biofuels production due to its availability in Malaysia. In Malaysia, several studies focus on palm oil based for biofuel production such as palm oil, palm kernel oil, used or waste cooking oil, and palm oil-based waste fatty acid (Ong and Bhatia, 2010). Spent bleaching earth (SBE) is one of the palm oil solid wastes or biomass that can be utilised to synthesise bio-hydrocarbons.

SBE can be defined as an industrial waste that is mainly generated from the edible oil processing. The bleaching process improves the appearance, flavour, taste and stability of the final palm oil products. However the bleaching process in palm oil refinery generates a large amount of SBE. SBE is commonly disposed in landfill without any pre-treatment and usually contains 20–40 wt% of residue oil (Tsai *et al.*, 2002). During the refining process, 0.5%–1.0% of activated clay or fresh bleaching earth (BE) is used where all BE will convert into waste as SBE and it is estimated that the production of SBE waste around the world is 600,000 tonne (Suhartini *et al.*, 2011). As the second largest producer of crude palm oil in the world, Malaysia alone produces more than 100,000 tonnes of SBE yearly which contains a high percentage of oil (Boey *et al.*, 2011). For this reason, it is potential to be used as a renewable raw material for the production of biofuel.

In Malaysia, as it is in many other countries, the SBE is still being disposed in landfills or dumping sites. The SBE normally contains residual oil, metallic impurities (Fe and Cu) and organic compounds that can cause environmental problems and increase the landfill disposal cost (Cheah and Siew, 2004). This disposal constituted a significant economic waste and an environmental burden (Nursulihatimarsyila *et al.*, 2010). Due to these problems, many researchers had attempted to improve the utilization of SBE as well as to extract the residual oil and regenerate the SBE (Boukerroui and Quali, 2000; Tsai *et al.*, 2000). Therefore, rather than being disposed and contributing to the pollution, this study proposes to recover the residue palm oil in SBE by catalytic cracking for both chemical and fuel application and regenerated SBE so that it can be used again.

The recovery of residual oils adsorbed in SBE as a biofuel has been studied by many researchers using solvent extraction, supercritical CO_2 extraction or lye extraction (Huang and Chang, 2010). Loh *et al.* (2006) used both solvent and supercritical fluid (SC-CO_2) extraction to recover oils from SBE generated at a palm oil refining industry. They found that those oils exhibited poor qualities in terms of free fatty acids content and peroxide value. Those oils were not suitable for food applications, but could be converted to their respective methyl esters for biodiesel applications (Huang and Chang, 2010). Kalam and Joshi (1988) indicated that SBE can be regenerated with the pretreatment of hexane extraction, and then reclaimed by an autoclave with the methods of wet oxidation or heating in aqueous medium. Waldmann and Eggers (1991) noted that SBE can be deoiled and thus regenerated by high-pressure extraction with supercritical CO_2. Low *et al.* (1996) pointed out that SBE can be carbonized with the methods as reported by Pollard *et al.* (1993) and then used as a sorbent. Ng *et al.* (1997) indicated that SBE can be initially deoiled by the solvent (i.e. hexane, methanol, and supercritical CO_2) extraction, and then regenerated by acid and heat treatments.

Biofuel production from palm oil based can be processed through a variety of routes depending on the targeted final products. For example, transesterification is only applied to the production of biodiesel whereas catalytic cracking can be applied for the production of gasoline, kerosene and diesel (Ong and Bhatia, 2008). Transesterification, pyrolysis and catalytic cracking conversion are the main routes proposed for the conversion of vegetable oils for biofuel (Botas *et al.,* 2012). Biodiesel is produced by transesterification of edible and non-edible oils with methanol or ethanol in the presence of catalyst (Kansendo *et al.,* 2009). The main drawback of transesterification using homogeneous catalysts is still the costs associated to the overall high energy consumption and separation (Chew and Bhatia, 2008). Moreover, biodiesel contains oxygen, gels state at cold temperature and its energy density is relatively low (Zhao *et al.,* 2012). The catalytic cracking process shows several clear advantages in comparison with the pyrolysis process. Firstly, catalytic cracking could be used to obtain a high yield of hydrocarbon biofuel from vegetable oil at a relatively lower reaction temperature (450^{o}C) than pyrolysis (500-850 ^{o}C). Next, catalytic cracking is a cost effective and simple technology to convert vegetable oil to hydrocarbon biofuel (Zhao *et al.,* 2012). In addition the product quality derived from pyrolysis is strongly dependent on the type of feedstock used (Ong and Bhatia, 2008). Hence, the alternative method for vegetable oil conversion to produce biofuel is catalytic cracking (Nam *et al.,* 2011). Botas *et al.* (2012) claimed that the catalytic cracking process presents advantages compared to transesterification and pyrolysis in terms of lower processing costs, feedstock flexibility and compatibility with already existing infrastructures. Moreover, catalytic cracking makes possible to enhance the selectivity toward desired products by the appropriate selection of the catalysts (Ong and Bhatia, 2010).

Particularly in Malaysia, significant research works have been done to convert palm oil based into biofuel hydrocarbons by using mesoporous catalysts in catalytic cracking (Twaiq *et al*., 2003 a,b, 2004; Ooi *et al*., 2003, 2004). In the first study by this research group, the catalytic cracking of palm oil was conducted in a fixed bed reactor at temperatures between 350-450 ^{o}C and atmospheric pressure. The catalysts used were HZSM-5, zeolite Beta, zeolite USY (Ultra-stable Y), hybrids of the three and HZSM-5 impregnated with potassium. The main findings were that among the HZSM-5, Zeolite B and USY catalysts, the HZSM-5 had the highest conversion and gasoline yield, lowest coke formation, and had the highest selectivity for aromatics, however, it also had the highest yield of gaseous hydrocarbons. The potassium impregnated catalysts were shown to decrease the aromatic content of the gasoline product, likely due to a change in the acidity of the catalyst. The gasoline yield was shown to increase when the HZSM-5-USY hybrid catalyst was used (Maher and Bressler, 2007). Hence, these findings show that HZSM-5 zeolite has good performance for the biofuels production from vegetable oils in catalytic cracking process.

Zeolite HZSM-5 is well known as an efficient catalyst for the catalytic cracking of petroleum based fuels due to its crystallinity, well-defined micropores, large surface area, interconnected network of channels, strong acidity and high resistance to deactivation. However, the chemical characteristics of residue palm oil in SBE are markedly different from those of petroleum oil. The relative narrow channels of zeolites lead to diffusional limitations and hinder the access to active catalytic sites for large reactants molecules such as triglycerides of palm oil. To overcome these inconveniences, metal-modified HZSM-5 zeolites have been extensively considered due to the high proportion of fully accessible catalytic sites located on the external surface (Botas *et al.*, 2012). The impregnation of transition metal to the catalyst such as HZSM-5 is expected to change the properties of catalysts in term of acidity and textural of the support changing its catalytic behaviour (Rahimi and Karimzadeh, 2011). The addition of metal into HZSM-5 zeolite also can leads to bi-functional catalysts. Botas *et al.* (2012) claimed that the catalytic cracking performance of the metal loaded on HZSM-5 zeolites can be determined by critical parameters like the metal site location and the metallic diffusion and sintering. Cracking of palm oil has been carried out by Achmad Roesyadi *et al.* (2013). They were recommended that Ni/HZSM-5 was the catalyst for cracking palm oil for the high selectivity to gasoline.

Therefore, catalytic cracking of palm oil based such as SBE has become more attractive and potential, as biofuel sources in Malaysia. Liquid biofuel are primarily used for fuel transportation vehicles, applicable to fuel engines or fuel cells for electricity generation (Ong and Bhatia, 2010; Botas *et al.*, 2012) and used as feedstock in the chemical industry for the production of lubricants, solvents, or lacquers (Maher and Bressler, 2007). Biofuel product can be easily stored and transported, readily upgraded and refined to produce high quality fuels, and may contain chemicals in economically recoverable amounts (Maher and Bressler, 2007). However, there are some limitations that may restrict the advantages of using biofuel for transportation vehicles and raw chemicals. The most crucial issue that should be highlight related to this study is the drawbacks that involved the biofuel quality product obtained from SBE pyrolysis and the efficiency of SBE regeneration in the recent studied.

1.2 Problem Statement

The recent study showed that pyrolysis of residual palm oil in SBE has the potential to produce both chemical and fuel (Boey *et al.*, 2011). However they reported that n-hexadecanoic acid were the major compounds found in the pyrolytic products analyzed using GC-MS. In this study they showed that overall the major classes of compound found in the pyrolysis products was a carboxylic acid with a mixture of aliphatic and oxygenated hydrocarbon components such as alcohols, ketones, aldehydes and esters. Significant amount of mono aromatic hydrocarbon (MAH) and polycyclic aromatic (PAH) also were found in Boey *et al.* (2011) study. It is evident that liquid mixtures with high percentages of hydrocarbons can be obtained by pyrolysis but in many of previous studies reported, undesirable, oxygenated compounds such as carboxylic acids and ketones still exist (Maher and Bressler, 2007). The major drawbacks of the liquid products as fuel from pyrolysis is that it is highly oxygenated, viscous, corrosive and thermally unstable (Adjaye and Bakhshi, 1995; Zhang *et al.*, 2007), while its high concentration of water and oxygenated compounds reduce its calorific value and change significantly the combustion characteristics. According to Williams and Nugranad (2000), the presence of certain undesirable oxygenated compounds (organic acids and carbonyls) and of polycyclic aromatic hydrocarbons (PAH), limits its potential for direct use in engines or turbines. The claims by these authors were similar results found by Boey *et al.* (2011) whereby n-hexadecanoic acid was the major oxygenated compound found in SBE pyrolysis product compound.

Besides, the production of biofuel from palm oil based using zeolite catalyst in catalytic cracking process has been widely studied. There are a few common types of zeolites, such as HZSM-5, β zeolite, γ zeolite, mordenite, silico alumino phosphate and several mesoporous materials in converting vegetable oil into biofuels (Majed and Tye, 2018). These kinds of catalysts show that zeolite possess a great potential as solid acid cracking catalyst due to its structure, acidity and high selectivity for the production of biofuels from vegetable oils. Meanwhile, catalytic cracking of palm oil over HZSM-5 was found to produce organic liquid rich in gasoline fraction from the catalytic cracking of palm oil based fatty acid mixture, however the selectivity for gaseous products was also high (Chang and Tye, 2013). Hence, the disadvantage using parent HZSM-5 catalyst has been improved by impregnated transition metal such as Cu, Ni and Zn into HZSM-5 catalyst for palm oil catalytic cracking (Roesyadi *et al.*, 2013). In this study, they reported that cracking palm oil increase gasoline yield results but decrease in kerosene and diesel yield.

SBE contains up to 40 % residual palm oil which can be vaporised and catalytically crack to produce chemical or biofuel. Furthermore the SBE obtained after pyrolysis can be regenerated. Very few studies are available in the literature regarding the regeneration of SBE from palm oil by pyrolysis at high temperature. Boukerroui *et al.*, (2017) reported that the SBE can be regenerated by heating at 350 °C for 1 h and the bleaching efficiency of regenerated SBE toward soybean oil was increased after its leaching by 1 M of hydrochloric acid (HCl) solution. However, until now there is no literature dedicate the regeneration of SBE in palm oil refineries in Malaysia at pyrolysis temperature (500 °C) for biofuel production followed with acid treatment (HCl or H_2SO_4). Therefore the regeneration of SBE after palm oil recovery is recommended.

Due to these problems, catalytic cracking of oil in SBE using HZSM-5 zeolite as a catalyst is introduced to enhance the production of biofuel which is expected to increase the amount of aliphatic and mono aromatic hydrocarbon (MAH). On the other hand, this catalytic cracking also expected to decrease amount of the oxygenated compounds and poly aromatic hydrocarbon (PAH). Catalysis plays important role in enhancing the triglycerides present in palm oil that can be converted into hydrocarbons through the removal of oxygen to produce liquid biofuel. In addition, Taufiqurrahmi *et al.* (2011) stated that in catalytic cracking processes, the palm oil containing triglycerides with long chain fatty acids are subjected to deoxygenation into short chain molecules, which are determined by both operating conditions and the properties of the catalysts. Among the different products that can be obtained, light olefins and aromatic hydrocarbons are particularly interesting due to their applications in the production of both raw chemicals and fuels (Botas *et al.*, 2012). To the best of our knowledge, there is lack of study on the catalytic cracking of residual palm oil from SBE using heterogeneous catalyst for the conversion into liquid products, therefore studies in this area are highly desired focusing on the SBE liquid products yield and regeneration of SBE.

1.3 Research Objective

Based on the research back ground and problem statement, the objectives of this research have been identified as follow:

1. To modify the zeolite HZSM-5 catalysts with transition metals and investigate the physicochemical properties of the modified catalyst for catalytic cracking.
2. To evaluate the performance of catalytic cracking of residual palm oil in SBE using zeolite HZSM-5 modified catalyst.
3. To investigate the effect of operating conditions and optimize the process conditions of catalytic cracking for optimum liquid products yield of residual palm oil in SBE.
4. To regenerate SBE toward BE properties and reused as a low cost mineral adsorbent.

1.4 Scope of Works

In order to achieve the aforementioned objectives, the following scopes are covered:

1. Modifying zeolite HZSM-5 catalyst with the identified transition metals such as Copper (Cu), Zink (Zn), Chromium (Cr) and Nickel (Ni) by wet impregnation method was carried out so that catalyst acidity and textural properties changes the catalytic behaviour. Then, characterization of the modified zeolites was conducted such as identifying the crystallinity of the each modified HZSM-5 catalyst with metals by using X-ray diffraction (XRD), identifying the functional groups exist in various impregnated metal HZSM-5 catalysts by using Fourier Transform Infra-Red (FTIR), measuring the surface area and micro pore volume (textural properties) of various impregnated metal HZSM-5 catalysts by using

nitrogen adsorption isotherm method and measuring the acidity of the catalyst by temperature programmed desorption of ammonia (TPD-NH_3).

2. Catalytic cracking of SBE was carried out in the fixed bed reactor to study the effect of the modified catalysts on process performance such as SBE conversion, liquid products yield and liquid products composition. Evaluating the production of liquid products yield and composition based on the chemical component exists, which will be determined by using Gas Chromatography-Mass Spectroscopy (GC-MS). After that, the most promising catalyst was selected.
3. By using the selected catalyst, studying the optimum operating conditions of liquid product yield was carried out by using central composite design (CCD) statistical software and investigating the interaction of process variables condition for optimum liquid product yield by using Responds surface methodology (RSM) in the range of temperature (400-500 ^{o}C), nitrogen flowrate (60-180 min), and heating time (60-100 mL/min).
4. Regenerating the SBE by pyrolysis process (500 ^{o}C) followed with varies (0.5, 1.0, 1.5, 2.0 and 3.0 M) sulphuric acid (H_2SO_4) concentration. After acid treatment, evaluating the adsorption capacity of regenerated spent bleaching earth (RSBE) for the crude palm oil (CPO) and methylene blue (MB) decolourisation by using spectrophotometer. Then, characterizing of physico-chemical properties of RSBE was carried out by using Themogravimetric (TGA), X-Ray diffraction (XRD), Fourier Transformed Infrared (FTIR), Nitrogen adsorption-desorption and Scanning electron microscopy **(**SEM) Analysis.

1.5 Significant of Study

The bulky nature, high residual oil content and increasing global production of SBE, a clayey waste material from edible oil processing industries, pose major disposal problems (Weng *et al.*, 2007). From the environmental, safety, and regulatory points of view, it is suggested to restrict the landfill practice in the future. Additionally, SBE as bio-feed can be the best choice to solve the competition between the use of vegetable oil as the source of food and fuel. Hence, it can be conclude that SBE is a cheap, abundantly available, excellent substrate for liquid product (biofuel) production. Up to date, no literature dedicated to an investigation of the catalytic cracking of residual palm oil in SBE by using HZSM-5 zeolite based catalyst has been reported.

In addition, the regeneration of SBE waste has aroused a great interest among many researchers which has been discussed previously. Majid and Mat (2017) reported that regeneration of SBE by impregnated SBE with sulphuric acid (H_2SO_4) and heat treatment exhibits a very promising performance in the decolourisation palm oil mill final effluent discharge. SBE was used to remove the colour and unstable impurities due to its high specific surface characteristic and relatively high adsorption performance for coloured materials and low purchasing cost (Bayrak, 2003). Similar to catalytic cracking study, there is also no literature dedicated to an investigation of palm oil SBE regeneration by pyrolysis at high temperature (>350 ^{o}C) for biofuel liquid production followed with H_2SO_4 solution treatment. Moreover, SBE is one of the promising adsorbents that can be considered as a potential adsorbent for methylene blue (MB) removal due to its low cost, availability (from edible oil refinery) and high sorption capacity (Low *et al.*, 1996). The results of this work could help decrease the cost of bleaching clay through recycling of SBE and recovering oil as well as reducing the environmental pollution problems resulting from the disposal of spent clay.

1.6 Thesis Outline

The thesis divided into 5 chapters. Chapter 1 describe briefly about research background, problem statement, objective and scope of work. In Chapter 2 a literature overview of vegetable oil and palm oil in pyrolysis and catalytic cracking. The focus lies on waste vegetable oil and waste palm oil as well as SBE. Chapter 3 describes the methodology which is used to modify zeolite catalysts and the designed reactor systems.

The physicochemical methods of modified HZSM-5 zeolite catalyst analysis and the evaluation of SBE catalytic cracking activity were also presented.

Finally residual palm oil in SBE catalytic cracking performance test was described. A study of the introduction of impregnated metals in HZSM-5 zeolite and characterization physico-chemical of the prepared catalysts were given in Chapter 4. The influence on the addition of metals on catalyst properties such as acidity, pore size and surface also was studied. In this chapter, an in-depth study of the effect of modified catalysts on residual palm oil SBE catalytic cracking performance is presented. The study emphasizes on the behaviour of the catalytic cracking activity to produce high yield hydrocarbon liquid products with significant parameters such as temperature, heating time and nitrogen flowrate. Response Surface Methodology (RSM) method was used for determining optimum amount of liquid products from catalytic cracking of residual palm oil in SBE. The studies continue with RSBE which SBE as a pollutant industrial waste that can be reused as a low cost mineral adsorbent. This topic focus lies on RSBE by pyrolysis and acid treatment. The performance of promising RSBE sample was tested with CPO and MB decolourisation.

Then the physicochemical properties of promising RSBE was studied and presented. Finally, in Chapter 5 conclusions on the promising developed zeolite catalyst and optimized liquid production from residual palm oil in SBE catalytic cracking are presented. Recommendations for further research are given as well as to upgrade the quality of liquid products similar with fossil fuel standard.

REFERENCES

Abnisa, F., Daud, W.M.A.W., Husin, W.N.W., Sahu, J.N. (2011) ‘ Utilization possibilities of palm shell as a source of biomass energy in Malaysia by producing bio-oil in pyrolysis process’, *Biomass and bioenergy*, 35, 1863-1872.

Aladetuyi, A., Olatunji, G.A., Ogunniyi, D.S., Odetoye , T.E, Oguntoy, S.O. (2014) ‘Production and characterization of biodiesel using palm kernel oil; fresh and recovered from spent bleaching earth’, *Biofuel Research Journal*, 4, 134 - 138.

Asadieraghi, M. and Daud, W.M.A.W. (2015) ‘In-situ catalytic upgrading of biomass pyrolysis vapor: Co-feeding with methanol in a multi-zone fixed bed reactor’, *Energy Conversion and Management*, 92, 448-458.

Al-zahrani, A.A. and Alhamed, Y.A. (1996) ‘Regeneration of spent bleaching clay by calcination cum-acid treatment’, *J. Indian Institute of Chem. Eng*, 38(3), 71-75.

Adjaye, J.D. and Bakhshi, N.N.(1995). Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part I: Conversion over various catalysts. *Fuel Process. Technol.* 45:161-183.

Argauer, Robert, J., Landolt, George, R. (1972) ‘Crystalline Zeolite ZSM-5 and Method of Preparing the Same’, *U.S. Patent,* 3, 702-886.

Al-Sabawi, M. and Chen, J. (2012) ‘Hydroprocessing of Biomass-Derived Oils and Their Blends with Petroleum Feedstocks: A Review’, *Energy Fuels*, 26, 5373-5399.

Anjos, D. J. R.S., Gonzalez, D.A.W, Lau, Y., Lam, R. (1983) ‘Catalytic decomposition of vegetable oil’, *Applied Catalysis*, 5, 299–308.

Aung, L.L., Tertre, E., Suksabye, P.,Worasith, N., Thiravetyan, P. (2015) ‘Effect of alumina content and surface area of acid-activated kaolin on bleaching of rice bran oil’, *J Am Oil Chem Soc*, 92, 295–304.

Bayrak, Y. (2003) ‘Adsorption isotherms in bleaching hazelnut oil’, *Journal of the American Oil Chemists' Society*, 80 (11), pp 1143–1146.

Baloch, H. A, Nizamuddina, S., Siddiquia, M.T.H., Riazb, S., Jatoib, A.S., Dumbrea, N.M. Mubarakc, D.K., Srinivasana, M.P., Griffina, M.T.H. (2018) ‘Recent advances in production and upgrading of bio-oil from biomass: A critical overview’, *Journal of Environmental Chemical Engineering*, 6, 5101–5118.

Ballmoos, R.V., Derouane, E.G., Fripiat, J.G. (1990) ‘Quantum mechanical calculations on molecular sieves. 2. Model cluster investigation of silicoaluminophosphates’, *The Journal of Physical Chemistry*, 94(4), 1687-1692.

Barrón A.E.C., Melo-Banda, J.A., Dominguez J.M. E., Hernández E.M., Silva R.R., Reyes A.I.T., Meraz M.A.M. (2011) ‘Catalytic hydrocracking of vegetable oil for agrofuels production using Ni–Mo, Ni–W, Pt and TFA catalysts supported on SBA-15’, *Catalysis Today,* 166, 102–110.

Boukerroui, A. and Ouali, M. S. (2000) ‘Regeneration of a Spent Bleaching Earth and Its Reuse in the Refining of Edible Oil’, *Journal of Chemical Technology and Biotechnology,* 75, 773-776.

Boukerroui, A., Belhocine, L., Ferroudj, S. (2017). ‘Regeneration and reuse waste from an edible oil refinery’, *Environmental Science and Pollution Research International*, 25(19), 18278-18285.

Bozbas, K. (2008). ‘Biodiesel as an alternative motor fuel: Production and policies in the European Union’, *Renewable and Sustainable Energy Reviews,* 12(2), 542-552.

Budianto, A., Prajitno, D.H., Roesyadi, A., Budhikarjono, K., (2014) ‘HZSM-5 Catalyst for Cracking Palm Oil to Biodiesel: A Comparative Study With and Without Pt and Pd Impregnation’, Scientific Study and Research: Chemistry and Chemical Engineering,15(1), pp. 081 – 090.

Buzetzki, E., ˇSvaˇnova,´ K., Cvengroˇsova,´ Z., Mikulec, J., Kaszonyi, A., Cvengroˇs, J. (2009) Liquid condensates from oil/fat cracking as components of blended diesel fuels. *In: Proceedings of the 44th international petroleum conference*. Bratislava, Slovak Republic: p.1–10.

Boey, P.L., Saleha, M.I., Sapawea, N., Ganesana, S.,Maniama, G.P., Mohamed Hag Ali, D. (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,* 91, 199-204.

Botas, J.A.,Serrano, D.P.,Garcíac, A., Vicentea, J.D.,Ramosa, R. (2012) 'Catalytic Conversion of Rapeseed Oil into Raw Chemicals and Fuels Over Ni- and Mo-modified nanocrystalline ZSM-5 zeolite', *Catalysis Today*, 195, 59-79.

Chang, W.H. and Tye, C.T. (2013) 'Catalytic Cracking of Used Palm Oil Using Composite Zeolite', *The Malaysian Journal of Analytical Sciences*, 17(1), 176-184.

Chew, T.L., Bhatia S. (2008) 'Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery', *Bioresource Technology*, 99(17), 7911-22.

Cheah, K. Y. and Siew, W.L. (2004) 'Regeneration of Spent Bleaching Clay', *Malaysian Palm Oil Board (MPOB) information series No.230*.

Chiam, L.T. and Tye, C.T. (2013) 'DeoxygenationoOf Plant Fatty Acid using NiSnK/SiO_2 as Catalyst', *The Malaysian Journal of Analytical Sciences*, 17(1), 129-138.

Chuaykleang, J. and Ratanawilai, S. (2014) 'Biogasoline from Catalytic Cracking of Refined Palm Oil using H-ZSM-5 Catalyst', *Int'l Journal of Advances in Chemical Engg.,& Biological Sciences (IJACEBS)*, 1(1), 1507-1515.

Corma, A., Huber, G.W., Sauvanaud, L., O'Connor, P. (2007) 'Processing biomass-derived oxygenates in the oil refinery: catalytic cracking (FCC) reaction pathways and role of catalyst, *Journal of Catalysis*, 247, 307-327.

Dandik, L., Aksoy, H.A., Erdem-Senatalar, A. (1998) 'Catalytic Conversion of Used Oil to Hydrocarbon Fuels in a Fractionating Pyrolysreactor', *Energy Fuels*, 12(6), 1148-1152.

Dandik, L. and Aksoy, H.A. (1998) 'Pyrolysis of used sunflower oil in the presence of sodium carbonate by using fractionating pyrolysis reactor', *Fuel Processing Technology*, 57, 81–92.

Damjanović, L. and Auroux, A. (2009) 'Determination of acid/base properties by temperature programmed desorption (TPD) and adsorption calorimetry', *In Zeolite characterization and catalysis*, 107-167.

Demirbas, A. (2007) 'Progress and Recent Trends in Biofuels', *Progress in Energy and Combustion Science,* 33, 1–18

Box, G.E.P., Hunter, W.G. and Hunter, J.S. (1978) *Statistics for experimenters*. John Wiley & Sons, Inc.

Folleto, E.L., Alves, C.C.A., Sganzerla, L.R., Porto, M.L. (2002) ‘Regeneration and Utilization of Spent Bleaching Clay’, *Latin American Applied Research*, 32, 205-208.

Franke, M.E., Simon, U. (2004) ‘Solvate supported proton transport in zeolites’, *Chem-PhysChem*, 5, 465‑472.

Fanchiang, W.L., Lin, Y.C. (2012) ‘Catalytic fast pyrolysis of furfural over HZSM-5 and Zn/H-ZSM-5 catalysts’, *Applied Catalysis A: General*, 419– 420,102–110.

Gary, J.H., Handwerk, G.E. (2001) *Petroleum Refining: Technology and Economics.* CRC Press.

Grieken, V., R., Sotelo, J.L., Menéndez, J.M., and Melero, J.A. (2000) ‘Anomalous crystallization mechanism in the synthesis of nanocrystalline ZSM-5’, *Microporous and Mesoporous Materials*, 39(1-2), 135-147.

Haaland, P.D. (1989) *Experimental Design in Biotechnology*. Marcel Dekker: New York.

Huber, G.W., Corma, A. (2007) ‘Synergies between bio- and oil refineries for the production of fuels from biomass’, *Angew. Chem. Int. Ed*., 46, 7184–7201.

Huang, Y.P., Chang J.I. (2010) ‘Biodiesel production from residual oils recovered from spent bleaching earth’, *Renewable Energy*, 35, 269–274.

Hou, S.C., Lin, C.I., Kuo, S.L. (1999) ‘Effect of Processing Condition on Regeneration of Bleaching Clays’, *J. Chin. Inst. Chem. Engrs*, 30, 501-506.

Idem, R.O., Katikaneni, S.P.R., Bakhshi, N.N.1996. ‘Thermal cracking of canola oil: reaction products in the presence and absence of steam’, *Energy Fuels*, 10,1150–1162.

Junming, X., Jianchun, J., Yanju, L., Jie, C. (2009) ‘Liquid hydrocarbon fuels obtained by the pyrolysis of soybean oils’, *Bioresource Technology*, 100, 4867–4870.

Junming, X., Jianchun, J., Yunjuan, S., Jie, C. (2010) ‘Production of hydrocarbon fuels from pyrolysis of soybean oils using a basic catalyst’, *Bioresource Technology*, 101, 9803–9806.

Jiang Y.J., Juan J.C., Meng X.J., Cao W.L.,Yarmo M.A., Zhang J.C. (2007) ‘Preparation and Catalytic Application of Novel Water Tolerant Solid Acid Catalysts of Zirconium Sulfate/HZSM-5’, *Chemical Research in Chinese Universities*, 23, 349‑354.

Kalam, A., Joshi, J.B. (1988) ‘Regeneration of Spent Earth by Oxidation’, *Journal of the American Oil Chemists’ Society*, 65(9), 1536-1540.

Kalnes, T., Marker, T. and Shonnard, D.R. (2007) ‘Green Diesel: A Second Generation Biofuel’, *International Journal of Chemical Reactor Engineering*, 5, A48.

Kansedo J, Lee KT, Bhatia S (2009) ‘Biodiesel production from palm oil via heterogeneous transesterification’, *Biomass and Bioenergy*, 33(2), 271–276.

Katikaneni, S.P.R., Adjaye, J.D., Bakhshi, N.N. (1995) ‘Catalytic Conversion of Canola Oil To Fuels and Chemicals over Various Cracking Catalysts’, *Canadian Journal of Chemical Engineering*, 73(4), 484–97.

Keshwani, D.R., Cheng, J.J. (2009) ‘Switchgrass for bioethanol and other value-added applications: a review’, Bioresour Technol., 100(4), 1515-1523.

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.

Kuck, J.C., Pons Jr., W.A . and Frampton, V.L. (1962) ‘Reactivation of alumina used in bleaching of off-colored cottonseed oils’, *J. Am. Oil Chem. Soc*, 39, 84.

Leng, T.Y., Mohamed, A.R., Bhatia, S. (1999) ‘Catalytic Conversion of Palm Oil to Fuels and Chemicals’, *The Canadian Journal of Chemical Engineering*, 77(1),156–162.

Leofantia, G., Padovanb, M., Tozzolac, G. (1998) ‘Surface area and pore texture of catalysts’, *Catalysis Today*, 41, 207-219.

Loh, S.K., Cheng, S.F., Choo, Y.M., Ma, A.N. (2006) ‘A Study of residual recovered from spent bleaching earth: their characteristics and applications’, *Am J Appl Sci.*, 3(10), 2063–2067.

Low, K.S., Lee, C.K., Wong, A.M. (1996) ‘Carbonized spent bleaching earth as a sorbent for some organic dyes’, *J. Environ. Sci. Health*, Part A, 31(3), 673-685.

Lowell, S. and Shields, J.E. (1991) *Powder Surface Area and Porosity*. Third ed., Chapman & Hall Ltd, London.

Maher, K.D., Bressler, D.C.(2007) ‘Pyrolysis of Triglyceride Materials for the Production of Renewable Fuels and Chemicals’, *Bioresource Technology,* 98, 2351–2368.

Maia, A. J., Louis, B., Lam, Y. L. and Pereira M. M. (2010) ‘Ni-ZSM-5 catalysts: Detailed characterization of metal sites for proper catalyst design’, *Journal of Catalysis,* 269(1), 103-109.

Mana, M., Ouali, M.S., De Menorval. L.C. (2007) ‘Removal of Basic Dyes from Aqueous Solutions with a Treated Spent Bleaching Earth’, *J. Colloid Interface Sci.*, 307, 9-16.

Majed, M.A.A. and Tye, C.T. (2018) ‘Catalytic Cracking of Used Vegetable Oil to Green Fuel with Metal Functionalized Zsm-5 Catalysts’, Malaysian Journal of Analytical Sciences, 22(1), 8-16.

Majid, R.A. and 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 (4), 579-587.

Meziti, C. and Boukerroui, A. (2011) ’Regeneration of a Solid Waste from an Edible Oil Refinery’, *Ceramics International*, 37, 1953-1957.

Melero, J.A., Iglesias, J.and Garcia, A. (2012) ‘Biomass as renewable feedstock in standard refinery units. Feasibility, opportunities and challenges’, *Energy & Environmental Science,* 5, 7379.

Montgomery, D.C. (1997) *Response Surface Methods and Other Approaches to Process Optimization*. In: Montgomery, D.C., Ed., Design and Analysis of Experiments, John Wiley & Sons, New York, 427-510.

Mohan, V., Raghavendra, C., Pramod, C.V., Raju, B.D., and Rama Rao, K.S. (2014) ‘Ni/H-ZSM-5 as a promising catalyst for vapour phase hydrogenation of levulinic acid at atmospheric pressure’, *RSC Advances.*, 4(19), 9660.

Montgomery, D.C. (2005) *Design and Analysis of Experiments*. 6th Edition, John Wiley & Sons, New York.

Mortensen, P.M. et al., (2011) ‘A review of catalytic upgrading of bio-oil to engine Fuels’, Appl. *Catal. A: Gen*. 407(1), 1–19.

Murata, K., Takahara, I. Inaba, M. (2008) ‘Propane Formation by Aqueous-Phase Reforming of Glycerol over Pt/H-ZSM5 Catalysts’, *React. Kinet. Catal. Lett.*, 93, 59-66.

Montgomery, D.C. (2006) *Design and Analysis of Experiments*. Wiley: New Jersey, USA.

Namchot, W. and Jitkarnka, S. (2015) 'Upgrading of waste tyre-derived oil from waste tyre pyrolysis over Ni catalyst supported on HZSM-5 zeolite', *Chemical Engineering Transactions*, 45, 775-780.

Ng, K.F., Nair, N.K., Liew, K.Y., Noor, A.M. (1997) 'Surface and Poor Structure of Deoiled Acid- and Heat- Treated Spent Bleaching Clays', *JAOCS*, 74(8), 963-969.

Ngo,T.A., Kim, J.,Kim, S.K., Kim, S.S.(2010). 'Pyrolysis of soybean oil with H-ZSM5 andMCM41 catalysts in a fixed-bed reactor', *Energy*, 35, 2723–2728.

Nam, L.T.H.,, Vinh, T.Q., Loan, N.T.T., Tho, V.D.S.,Yang, X.Y., Su B.L. (2011) 'Preparation of bio-fuels by catalytic cracking reaction of vegetable oil sludge', *Fuel*, 90, 1069–1075.

Nursulihatimarsyila, A.W., Cheah, K.Y., Chuah, T.G., Siew W.L., Choong, T. S.Y. (2010) 'Deoiling and Regeneration Efficiencies of Spent Bleaching Clay', *American Journal of Applied Sciences*, 7(3), 434-437.

Ong, Y.K., Bhatia S. (2010) 'The current status and perspectives of biofuel production via catalytic cracking of edible and non-edible oils', *Energy*, 35,111–119

Omar, W.N.N.W and Amin, N.A.S. (2011). 'Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology', *Biomass and bioenergy*, 35(3), 1329-1338.

Ooi, Y.S., Twaiq, F.A., R., Mohamed, A.R., Bhatia, S. (2003) 'Biofuel production from catalytic cracking of palm oil', *Energy Sources*, 25, 859–869.

Ooi, Y.S., Zacharia, R., Mohamed, A.R., Bhatia, S. (2004) 'Hydrothermal stability and catalytic activity of mesoporous aluminum-containing SBA-15', *Catalysis Communications*, 5, 441–445.

Phiwdang, K., Suphankij, S., Mekprasart, W. and Pecharapa, W. (2013) 'Synthesis of CuO Nanoparticles by Precipitation Method Using Different Precursors', *Energy Procedia*, 34, 740.

Pollard, S.J.T., Sollars, C.J., Perry, R. (1993) 'The reuse of spent bleaching earth: a feasibility study in waste minimization for the edible oil industry', *Bio resource Technology*, 45, 53-58.

Prado, C. M. R. and Filho, N. R. A. (2009) ‘Production and characterization of the biofuels obtained by thermal cracking and thermal catalytic cracking of vegetable oils’, *Journal of Analytical and Applied Pyrolysis*, 86 (2), 38-347.

Pizarrro, A.V.L. and Park, E.Y. (2003) ‘Lipase-catalyzed production of biodiesel fuel from vegetable oil contained in waste activated bleaching earth’, *Process Biochem.*, 38, 1077–82.

Quesada, D. E. and Iglesias, F. A. C. (2014) ‘Utilisation of Spent Filtration Earth or Spent Bleaching Earth from the Oil Refinery Industry in Clay Products’, *Ceramics International*, 40, 16677-16687.

Qiu, Y., Zhao, G., Liu, G., Wang, L., and Zhang, X. (2014)‘Catalytic cracking of supercritical n-dodecane over wall-coated nano-Ag/HZSM-5 zeolites*’, Industrial & Engineering Chemistry Research*, 53(47), 18104-18111.

Rahimi and Karimzadeh, R. (2011) ‘Catalytic Cracking of Hydrocarbons over Modified ZSM-5 Zeolites to Produce Light Olefins: A Review, *Applied Catalysis A: General*, 398, 1-17.

Ramya, G., Sudhakar, R., Amala, J., Joice, I., Ramakrishnan, R., Sivakumar, T. (2012) ‘Liquid hydrocarbon fuels from jatropha oil through catalytic cracking technology using AlMCM-41/ZSM-5 composite catalysts’, *Applied Catalysis A: General*, 433–434, 170–178.

Roesyadi, A., Hariprajitno, D., Nurjannah, N., Savitri, S.D. (2013) ‘HZSM-5 Catalyst for Cracking Palm Oil to Gasoline: A Comparative Study with and without Impregnation’, *Bulletin of Chemical Reaction Engineering & Catalysis*, 7(3), 185-190.

Ruddy, D.A, Schaidle, J.A, Ferrell, J.R., Wang, J., Moens, L. and Hensley, J.E. (2014) ‘Recent advances in heterogeneous catalysts for bio-oil upgrading *via* “*ex situ* catalytic fast pyrolysis”: catalyst development through the study of model compounds’, *Conversion of biomass with heterogeneous catalysts*, 16, 454-490

Rodríguez-González, L., Hermes, F. Bertmer, M., Rodríguez-Castellón, E., Jiménez-López, A. Simon, U. (2007) ‘The Acid Properties of HZSM-5 as Studied by NH_3-TPD and 27 Al-MAS-NMR Spectroscopy’, *Appl. Catal. A: Gen.*, 328, 174‑182.

Sannita, E., Aliakbarian, B., Casazza, A.A., Perego, P., Busca., G. (2012) ‘Medium-temperature conversion of biomass and wastes into liquid products, a review’, *Renewable and Sustainable Energy Reviews,* 16, 6455–6475.

Siregar, T.B., Amin, N.A.S. (2006) ‘Catalytic Cracking of Palm Oil To Gasoline Over Pretreated Cu–ZSM–5’, *Jurnal Teknologi*, 44, 69-82.

Subsadsana, M., Ruangviriyachai, C. (2016) ‘Effect of NiW Modified HZSM-5 and HY Zeolites on Hydrocracking Conversion of Crude Palm Oil to Liquid Hydrocarbons’, Oriental Journal of Chemistry, 32(2), 839-844.

Szostak, R. (1991) ‘Chapter 5 Modified Zeolites’, *Studies in Surface Science and Catalysis,* 58, 153-199.

Suprum, W., Lutecki, M., Haber, T., Papp, H. (2009) ‘Acidic Catalysts for the Dehydration of Glycerol: Activity and Deactivation’, *J. Mol. Catal., A: Chem*, 309, 71‑78.

Suhartini, S., Hidayat, N., Wijaya, S. (2011) ‘Physical Properties Characterization of Fuel Briquette Made from Spent Bleaching Earth’, *Biomass and Bioenergy,* 35, 4209-4214.

Suurs, A.A.R., Hekkert, M.P. (2009) ‘Competition between First and Second Generation Technologies: Lessons from the Formation of a Biofuels Innovation System in the Netherlands’, *Energy,* 34, 669–79.

Scherzer, J. (1990) *Octane-enhancing Zeolitic FCC Catalysts*. Marcel Dekker, New York.

Silva, S.M., Sampaio, K.A., Ceriani, R., Verhé, R., Stevens, C., De Greyt, W., Meirelles, A.J.A (2013) ‘Adsorption of carotenes and phosphorus from palm oil onto acid activated bleaching earth: equilibrium, kinetics and thermodynamics’, *J. Food Eng,* 118,341–349.

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 Sci Technol, 59,1258–1264.

Taufiqurrahmi, N., Mohamed, A.R., Bhatia, S. (2011) ‘Production of biofuel from waste cooking palm oil using nanocrystalline zeolite as catalyst: Process optimization studies’, *Bioresource Technology,* 102, 10686–10694.

Thanh-An, N., Kim, J., Kim S.K., Kim S.S. (2009) ‘Pyrolysis of Soybean Oil with H-ZSM-5 (proton–exchange of zeolite socony mobil#5) and MCM-41 (mobilecomposition of matter No.41) catalysts in a fixed bed reactor’, *Energy*, 1–6.

Twaiq, F.A., Mohamad, A.R., Bhatia, S. (2004) ‘Performance of composite catalysts in palm oil cracking for the production of liquid fuels and chemicals’, *Fuel Process. Technol.*, 85 (11), 1283–1300.

Twaiq, F.A., Mohamed, A.R., Bhatia, S. (2003a) ‘Liquid hydrocarbon fuels from palm oil by catalytic cracking over aluminosilicates mesoporous material withvarious Si/Al ratios’, *Micropor. Mesopor. Mater*, 64, 95–107.

Twaiq, F.A., Zabidi, N.A.M., Mohamed, A.R., Bhatia, S. (2003b) ‘Catalytic conversion of palm oil over mesoporous aluminosilicates MCM-41 for the production of liquid hydrocarbon fuels, *Fuel Process. Technol.*, 84, 105–121.

Twaiq, F.A., Zabidi, N.A.M., Bhatia, S. (1999) ‘Catalytic conversion of palm oil to hydrocarbons: performance of various zeolite catalysts’, *Ind. Eng. Chem. Res.*, 38,3230–3238.

Tsai, W.T., Chen, H.P. , Hsieh, M.F., Sun, H.F., Chien, S.F. (2002) ‘Regeneration of Spent Bleaching Earth by Pyrolysis In A Rotary Furnace’, *J. Anal. Appl. Pyrol.*, 63,157–170.

Tsai, W.T., Chen, H.P., Hsien, W.Y., Lai, C.W., Lee, M.S. (2003) ‘Thermochemical, Regeneration of Bleaching Earth Waste with Zinc Chloride’, *Resources conservation recycling*, 39:65-77.

Werner, Z., Prado, F.L. (1994) ‘Safety and environment’, *Int. News Fats Oils Relat. Mater*’, 5,1375-1383.

Waldmann, C.,Eggers, R.(1991) ‘Deoiling and Regeneration Efficiencies of Spent Bleaching Clay, *J. Am. Oil Chem. Soc.*, 68, 922–930.

Wambu, E.W., Muthakia, G.K., wa-Thiong'o, J,K., Shiundu, P.M. (2009) ‘Regeneration of spent bleaching earth and its adsorption of copper (II) ions from aqueous solutions Applied Clay Science, 46, 176–180.

Wang, X.J. (2007) ‘Reclamation of soybean oil residues’, *China Resour. Compr. Util*, 125, 15-17.

Wang, X.H., Si, N., Ye, A.Y., Yao, C. (2006) ‘Comprehensive utilization of vegetable oil residue’, *Mod. Chem. Ind.*,26, 21-24.

Weng, C.H., Tsai, C.Z., Chu, S.-H., Sharma, Y.C. (2007) ‘Adsorption Characteristics of Copper (II) onto Spent Activated Clay. Separation and Puriffication Technology’, 54, 187-197.

Wiggers, V.R., Meier, H.F., Wisniewski Jr., A., Barros A.A.C, Maciel, M.R.C. (2009) ‘Biofuels from continuous fast pyrolysis of soybean oil: a pilot plant study, *Bioresource Technology*, 100, 6570–6577.

Wong, S. L., Abdullah, T.A.T., Ngadi, N., Ahmad, A. and Inuwa I. M. (2016) ‘Parametric study on catalytic cracking of LDPE to liquid fuel over ZSM-5 zeolite’, *Energy conversion and management,* 122, 428-438.

Wu, X. (2003) *Acidity and catalytic activity of zeolite catalysts bound with silica and alumina*. PhD Thesis, Texas A&M University.

Williams, P.T., Nugranad, N. (2000) ‘Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks’, *Energy,* 25, 493–513.

Xiong, X., Li, X., Xiang, J., Wu, Q. (2008) ‘High-Density Fermentation of Microalga Chlorella protothecoides in Bioreactor for Microbio-Diesel Production Appl. Microbiol’, *Biotechnol*.,78, 29–36.

Xu, J., Jiang, J., Sun, Y., Chen, J., ‘Production of hydrocarbon fuels from pyrolysis of soybean oils using a basic catalyst’, *Bioresour Technol,* 101(24), 9803-9803.

Zakaria, Z.Y., Linnekoski, J.,S.Amin, N.A. (2012) ‘Catalyst screening for conversion of glycerol to light olefins’, *Chemical Engineering Journal,* 207-208, 803-813.

Zaki, I., Abdel-Khalik, M., Habashi, G.M. (1986) ‘Acid leaching and consequent pore structure and bleaching capacity modifications of Egyptian clays’, *Colloid Surf* , 17,241–249.

Zhang, Q., Chang, J., Wang, T.J., Xu, Y. (2007) ‘Review of biomass pyrolysis oil properties and upgrading research’, *Energy Convers. Manage,* 48, 87-92.

Zhou, H., Wu, C., Onwudili, J.A., Meng, A., Zhang, Y., and Williams, P.T. (2015) ‘Polycyclic aromatic hydrocarbons (PAH) formation from the pyrolysis of different municipal solid waste fractions’, *Waste Management,* 36, 136-146.

Zhao, X., Wei, l. Julson, J.,Qiao, Q., Dubey, A. and Anderson, G. (2015) ‘Catalytic cracking of nonedible sunflower oil over ZSM-5 for hydrocarbon bio-jet fuel’, *New biotechnology,* 32(2), 300-312.

Zhao, X., Wei, L., Cheng, S., Julson, J., Anderson, G., Muthukumarappan, K., Qiu, C. (2016) ‘Development of Hydrocarbon Biofuel From Sunflower Seed and Sunflower Meat Oils over ZSM-5’, *J. Renew. Sustain. Energy*, 8, 013109.

Zhao, X., Wei, L., Cheng, S., and Julson, J. (2017) ‘Review of Heterogeneous Catalysts for Catalytically Upgrading Vegetable Oils into Hydrocarbon Biofuels’, *Catalysts*, 7, 83.