INFLUENCE OF ALKALI AND ALKALINE EARTH METALS ON PYROLYSIS OF PALM KERNEL SHELL

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ABSTRACT

Pyrolysis is a promising technology for the production of renewable fuels and chemicals from high-lignin biomass. With the growing interest in utilizing lignin, using cheap and naturally available catalyst such as alkali and alkaline earth metals (AAEM) has becoming more attractive. However, significant knowledge on how it influences the thermochemical reaction during the pyrolysis process is still lacking and questionable. Thus, this study aimed to investigate how the AAEM influences the pyrolysis of palm kernel shell (PKS), a biomass feedstock with high lignin content which is vastly available in Malaysia. The untreated, treated and salt impregnated PKS samples were used in this study. The treated PKS was prepared using mild acetic acid, soaked with solutions at 50°C. The impregnation of AAEM on treated PKS was achieved by using chloride salts of Na, K, Mg and Ca. The research starts with a physicochemical analysis of PKS focusing on the influence of particle size on AAEM concentrations (dpA: <0.3mm, dpB: 0.3-0.7mm, dpC: 0.7-1mm, dpD: 1-2mm). The results show that smaller particle size exhibited higher ash and AAEM content. The second objective is to analyse the thermal degradation of all investigated PKS samples via thermogravimetric analysis (TGA). TGA analysis showed that the char residue at 900°C was the least for PKS sample size (dp) from treated PKS dpD* and untreated PKS dpA (11.3 mass%) while dpB, dpC and dpD had higher char residue (26.3 mass%). Maximum degradation temperature of PKS impregnated with Ca in hemicellulose region reduced from 307 to 248°C while in the presence of K, the temperature reduced from 300 to 276°C. The third objective is to investigate the effect of AAEM on pyrolysis product yield and composition of pyrolysis oil from all types of PKS sample. The result showed that the treated PKS produced the highest oil yield at 500°C (52.4 wt.%) compared to untreated PKS (46.7 wt.%). From composition analysis of pyrolysis oil, the presence of alkali metals promoted the production of catechols and syringols while the presence of alkaline earth metals suppressed the production of catechols, syringols and guaiacols in pyrolysis oil. The fourth aim is to determine the most suitable kinetic method to predict the kinetic parameters for treated PKS samples. By using experimental data from TGA analyzer, three kinetic methods (Reaction rate constant, Doyle's approximation and Murray and White's approximation) were evaluated and the method with the least mean squared error value was selected to determine the kinetic parameters of the PKS impregnated with Ca. The results showed that Murray and White's approximation is the most suitable kinetic method with the least mean squared error less than 0.5. The fifth objective is to correlate the pyrolysis reaction rate with different concentration of Ca in treated PKS. Using kinetic parameters calculated from Murray and White's approximation and a modified Langmuir Hinshelwood relation, three models were developed based on hemicellulose, cellulose and lignin thermal degradation temperature range. The result showed that hemicellulose and cellulose models were successful in predicting the pyrolysis reaction rate of PKS impregnated with Ca up to 6% for thermal degradation that occurred between 290 and 365°C.

ABSTRAK

Pirolisis adalah teknologi yang berpotensi untuk penghasilan bahan api dan bahan kimia diperbaharui daripada biojisim jenis tinggi lignin. Dengan peningkatan minat dalam menggunakan lignin, penggunaan mangkin yang murah dan tersedia secara semula jadi seperti logam alkali dan alkali bumi (AAEM) menjadi lebih menarik. Namun masih ada jurang kefahaman yang besar dalam memahami bagaimana lignin mempengaruhi tindak balas termokimia semasa proses pirolisis. Oleh itu, kajian ini bertujuan untuk mengkaji bagaimana AAEM mempengaruhi pirolisis tempurung kelapa sawit (PKS), iaitu sejenis biojisim dengan kandungan lignin yang tinggi yang banyak terdapat di Malaysia. Sampel PKS tanpa dirawat, terawat dan diisi tepu dengan AAEM telah digunakan dalam kajian ini. Sampel PKS terawat disediakan dengan merendam sampel di dalam larutan asid asetik lemah pada 50°C. Pengisian tepu AAEM pada PKS terawat dicapai dengan menggunakan garam klorida logam Na, K, Mg dan Ca. Kajian ini dimulai dengan analisis fizikokimia PKS dengan tumpuan terhadap kesan saiz partikel kepada kandungan kepekatan AAEM (dpA: <0.3mm, dpB: 0.3-0.7mm, dpC: 0.7-1mm, dpD: 1-2mm). Hasil kajian menunjukkan bahawa saiz partikel yang lebih kecil menunjukkan kandungan abu dan kepekatan AAEM yang lebih tinggi. Objektif kedua adalah untuk mengkaji penguraian terma sampel PKS melalui analisis termogravimetri (TGA). Analisis TGA menunjukkan kandungan abu pada 900°C adalah paling sedikit untuk PKS terawat dpD* dan PKS tanpa dirawat dpA (11.3% jisim) manakala PKS tanpa dirawat dpB, dpC dan dpD mempunyai sisa arang yang tinggi (26.3% jisim). Suhu maksimum penguraian terma bagi sampel PKS isian tepu dengan logam Ca bagi hemiselulosa menurun dari 307 ke 248°C sementara dengan kehadiran K, suhu berkurang dari 300 ke 276°C. Objektif ketiga adalah untuk mengkaji kesan kehadiran AAEM pada hasil produk pirolisis dan komposisi minyak pirolisis dari semua sampel PKS. Keputusan menunjukkan sampel PKS terawat menghasilkan hasil minyak tertinggi pada suhu 500°C (52.4% jisim) berbanding dengan PKS tanpa dirawat (46.7% jisim). Daripada analisis komposisi minyak pirolisis, kehadiran logam alkali meningkatkan penghasilan catechols dan syringols manakala kehadiran logam alkali bumi merencatkan penghasilan catechols, syringols dan guaiacols dalam minyak pirolisis. Objektif keempat adalah untuk menentukan kaedah kinetik yang paling sesuai untuk menjangkakan parameter kinetik sampel PKS terawat. Menggunakan data dari analisis TGA, tiga kaedah kinetik (pemalar kadar tindak balas, penghampiran Doyle dan penghampiran Murray dan White) telah dinilai dan kaedah dengan nilai ralat min kuasa dua terendah akan dipilih sebagai kaedah kinetik paling sesuai. Keputusan menunjukkan kaedah penghampiran Murray dan White adalah yang paling sesuai dengan nilai ralat min kuasa dua kurang daripada 0.5. Objektif kelima adalah untuk mencari korelasi antara kadar tindak balas pirolisis dengan kepekatan Ca yang berbeza pada sampel PKS terawat. Menggunakan parameter kinetik daripada kaedah penghampiran Murray dan White serta hubungan Langmuir Hinshelwood yang diubah, tiga model telah dibangunkan berdasarkan julat suhu perguraian terma hemiselulosa, selulosa dan lignin. Keputusan menunjukkan bahawa model hemiselulosa dan selulosa berjaya menjangkakan kadar tindak balas pirolisis yang paling hampir dengan nilai kadar tindak balas asal pada sampel PKS diisi tepu dengan Ca sehingga 6% untuk degradasi terma yang berlaku diantara 290 dan 365°C.

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LIST OF ABBREVIATIONS

A	-	Pre-exponential factor
AAEM	-	Alkali and alkaline earth metal
Al	-	Aluminum
Ca	-	Calcium
$CaCl_2.2H_20$	-	Calcium dihydrate
Cl	-	Chlorine
Cl^-	-	Chloride ion
CO_3^{2-}	-	Carbonate ion
E	-	Activation energy
Fe	-	Iron
GC-MS	-	Gas Chromatography-Mass Spectrometry
HZSM-5	-	Hydrogen exchanged Zeolite Socony Mobile Five
K	-	Potassium
KCl	-	Potassium chloride
LH	-	Langmuir-Hinshelwood
Mg	-	Magnesium
$MgCl_2.6H_2O$	-	Magnesium chloride hexahydrate
MW	-	Murray and White’s approximation
N	-	Nitrogen
Na	-	Sodium
NaCl	-	Sodium chloride
OH	-	Hydroxide
PKS	-	Palm kernel shell
RCM	-	Reaction rate constant method
RMSE	-	Root mean square error
S	-	Sulphur
TGA	-	Thermogravimetric analysis
Ti	-	Titanium

LIST OF SYMBOLS

K	-	Kelvin
R^2	-	Coefficient of determination
wt.%	-	Weight percent
h	-	Hour
db	-	Dry basis
dP	-	Particle size

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CHAPTER 1

INTRODUCTION

Renewable energy is the fastest-growing energy source globally where it makes up 26.2 percent of global electricity generation in 2018 (*Renewables 2019 Global Status Report*, 2019). It is also estimated that, by 2025, over 15% of the three trillion dollar global chemical sales will be derived from bio-based sources (Vijayendran, 2011). Due to the abundance and carbon-neutral nature, biomass, therefore, is a promising resource of renewable energy (Dhyani and Bhaskar, 2018a). Consecutively, biomass conversion technology such as pyrolysis, gasification and combustion has been vastly studied to meet the growing demand for replacements for petroleum-based fuels and products.

Concerning the production of chemicals from bio-based sources, the absence and presence of alkali and alkaline earth metal (AAEM) in the biomass ash have become a research topic for biomass-related research. Most of the research has been focusing on how the AAEM affects the pyrolysis product yield, kinetics and pyrolysis oil chemical compositions. Some of the high-value chemical components which can be found in pyrolysis oil from pyrolysis of biomass are acetic acid and furfurals from hemicellulose, levoglucosan and hydroxyacetaldehyde from cellulose and phenols and methanol from lignin degradation (Wild et al., 2011)

In studying the effect of AAEM during pyrolysis of biomass, alkali metal presence such as sodium (Na), produces more furan, acids, ketones and phenols compared to its absence in the pyrolysis oil composition from rice straw and bamboo (Lou et al., 2013). The removal of alkali metals (Na, K) however increased the concentrations of levoglucosan, a high-value chemical component in pyrolysis oil (Fahmi et al., 2007). Previous research also has reported on the potassium (K) addition as a catalyst during pyrolysis which could restrain the formation of volatiles and lower the initial temperature pyrolysis and the weight loss rate (Eom et al., 2011). In the kinetic analysis, its presence during pyrolysis also reported reducing the average apparent activation energy for willow coppice pyrolysis by up to 50 kJ/mol (Nowakowski et al., 2007).

For alkaline earth metals, calcium oxide for example which presence in biomass ash is responsible for enhancing the production of high-value gases such as hydrogen, which makes it an attractive low-cost material to be used as a catalyst (Gan et al., 2018). Utilizing bio-char of seaweed on pyrolysis of green macroalgae has also reported promoting hydrogen-rich gas and phenolic-rich pyrolysis oil (Norouzi et al., 2016). For biomass with high lignin content such as palm kernel shell (PKS), the main chemical component is phenol which is considered as one of the high-value chemical components in pyrolysis oil. Phenolic-rich pyrolysis oil has also been studied for the synthesis of phenolic resin (Choi et al., 2015; Sukhbaatar et al., 2009).

Apart from the analysis on how concentrations of AAEM affect the thermal degradation and kinetic parameters during the pyrolysis of biomass, researchers have been focusing on finding the relations between the AAEM concentration with the concentrations of chemical components in the pyrolysis oil. For example, the effects of K, Mg and Ca presence at different concentrations towards glycoaldehydes, acetic acid, acetol, butanediol, levoglucosan, furans, pyrans and cyclopentenes (Eom et al., 2012). Other than that, nickel and iron impregnated on cellulose, xylan and lignin at different concentrations showed that both metals promote the formation of char and inhibit the depolymerization of cellulose. However, in the lignin matrix, both metal presence decreases the concentration of aromatic compounds (Collard et al., 2012)

In this research, the focus was on the catalytic effects of AAEM on the pyrolysis process using PKS due to its high-lignin component compared to wood based biomass and other agricultural residue such as corn stover, sugarcane bagasse and pineapple waste. Influence of AAEM on the pyrolysis kinetics parameters was studied to investigate how AAEM affect thermal degradation of biomass at different concentration. Finally, a correlation between the AAEM concentration and the pyrolysis reaction rate was done and the results were evaluated.

1.1 Problem statement

Efficient utilization of biomass waste from agricultural sectors to biofuel and high-value chemical building blocks is one of the great measures to boost the country's agricultural economy, waste management and reduce our dependency on non-renewable fossil fuel and petrochemical derivatives. In Malaysia alone, a huge quantity of lignocellulose biomass is produced annually from the palm oil plantation. In 2015, the solid biomass waste (palm fronds, palm trunks, empty fruit bunches, mesocarp fibers and palm kernel shells) generated in Malaysia was rated about 75.61 million tonnes per annum (Dalton et al., 2017). Palm kernel shells (PKS) alone stand for 1.20 tonnes per hectare in dry fresh fruit bunch (FFB) basis which represents 11.4% FFB (Abdullah and Sulaiman, 2013).

PKS is a suitable biomass feedstock for pyrolysis due to its moisture content was reported to be lower than 10-14% (Danish et al., 2015). Commercialization of pyrolysis oil as biofuel or chemical building blocks has been long-awaited since there is an increase in awareness to shift to cleaner fuel options. Such achievement would also allow us to produce our own sustainable and renewable chemicals and materials. With high lignin content (44.0-50.7%), the valorization of chemicals such as phenols and aromatic components from PKS is an interesting aspect to be considered (Nizamuddin et al., 2016).

Using pyrolysis technology to convert PKS to pyrolysis products, AAEM which exists naturally in the biomass ash has the potential to act as a natural catalyst to enhance or inhibit certain chemical components in the pyrolysis oil (Eom et al., 2012). Besides that, AAEM also influences the pyrolysis product yield, thermal degradation curve and kinetics during pyrolysis (Kim et al., 2019; Shi et al., 2012). In analyzing the influence of AAEM on biomass pyrolysis, previously published studies were mostly focused on the effect of alkali metals on cellulose pyrolysis (Patwardhan et al., 2010a). The increase in the influence of alkaline earth metals especially on lignin components would have made the studies more relevant as there is an increase in lignin valorization for chemical building blocks (Custodis et al., 2015; Ľudmila et al., 2015).

In kinetics analysis, research on this subject has been mostly restricted to analyze kinetic parameters and comparison of kinetic methods (Ma et al., 2016). The study would have been more interesting if the pyrolysis reaction rates can be analyzed using the kinetic parameters which would contribute to the design of a larger scale pyrolysis reactor. Apart from that, the influence of AAEM concentration was mostly carried out to predict the trend of chemical concentrations which has been producing contradictory results between researchers due to the complex pyrolysis oil composition and the variety of biomass feedstocks (Eom et al., 2012).

Therefore, this research proposed to utilize the palm kernel shell to provide significant insights on how both alkali and alkaline earth metals influence the pyrolysis of high-lignin biomass waste based on physicochemical properties, thermal degradation, chemical composition and product yield. In the kinetic analysis, three kinetics methods (Reaction rate constant method, Doyle's approximation, Murray and White approximations) were evaluated and compared to find the methods with the least error for PKS pyrolysis. The selected method was then used to calculate the kinetics parameters of metal impregnated PKS where a correlation between the chosen metal concentrations and the pyrolysis reaction rates were studied using a method that combines kinetics approach and a modified Langmuir-Hinshelwood relation.

1.2 Research objectives

The main objective of this research is to investigate the catalytic effects of alkali and alkaline earth metals (AAEM) in palm kernel shell (PKS) using pyrolysis. The following sub-objectives are identified to achieve this objective.

1. To characterize the physicochemical properties of untreated PKS at various particle size and treated PKS at one selected particle size.
2. To analyze the effect of AAEM on thermal degradation of untreated, treated and metal impregnated PKS at one particle size.

3. To investigate the effect of AAEM on pyrolysis product yield and composition of pyrolysis oil.

4. To determine the most suitable kinetic method to predict the kinetic parameters of treated PKS.

5. To correlate the pyrolysis reaction rates with the calcium concentrations through calcium impregnated PKS at various concentrations.

1.3 Research scopes

To achieve the objectives, the following scopes have been identified.

1. Biomass characterization via CHNS analyzer (ultimate analysis), thermogravimetric analyzer (proximate analysis) and inductively coupled plasma optical emission spectrometry (ICP-OES) for metal analysis. The untreated PKS consists of four particle size ranges; 1-2 mm, 0.73-1 mm, 0.3-0.7 mm and less than 0.3 mm.

2. Biomass pretreatment to remove AAEM using the acetic acid washing method. Then, the characterization of treated PKS was performed for sample size 1-2mm.

3. Biomass impregnation using treated PKS impregnated with chloride salts of Na, K, Mg and Ca at 1 wt.% concentration for thermogravimetric analysis and pyrolysis experiment using sample size 1-2mm. Treated PKS impregnated with chloride salt of calcium for correlation analysis at 0.1, 0.3, 0.5, 1.0 and 3.0 % Ca.

4. Thermogravimetric analysis of untreated PKS, treated PKS and K and Ca impregnated PKS.

5. Conduction of pyrolysis experiment using untreated, treated and AAEM impregnated PKS at various temperatures (400-600°C) for pyrolysis product yield and characterization of pyrolysis oil chemical composition.

6. Kinetic parameters analysis (activation energy, Ea and pre-exponential factor, A) via reaction rate constant method (RCM), Doyle's approximation and Murray and White's temperature integral approximations using treated PKS.

7. Correlation between pyrolysis reaction rate and calcium's concentrations via Murray and White's approximation and modified Langmuir-Hinshelwood relation.

1.4 Significance of the study

The findings of this study will redound to the benefit of the commercialization of biofuel and chemical building blocks from biomass at the industrial level. The research utilized the palm kernel shell as a biomass feedstock which contains a high level of lignin. The removal and addition of AAEM from the PKS would allow a better understanding of the influence of individual AAEM towards physicochemical properties, chemical compositions and pyrolysis product yield. The kinetic methods evaluation between reaction rate constant method (RCM) and two temperature integral of the Arrhenius namely Doyle's and Murray and White's approximation would allow identifying the kinetic method which produces the least mean squared error (MSE) for pyrolysis of PKS. MSE value is a measure of a model's performance where a lower MSE value indicates a better model fit. Integrating the kinetic method and the modified Langmuir-Hinshelwood relation would then create an opportunity to analyze the pyrolysis reaction rate value at different AAEM concentrations. Moreover, using a high-lignin feedstock would benefit in terms of wider temperature range selection for kinetic analysis as the strong lignin bonding would result in a well-defined hollocellulose peaks during thermal degradation analysis. Hence, these would contribute to the body of knowledge on the influence of AAEM on biomass pyrolysis specifically in understanding the catalytic effect of AAEM for future pyrolysis reactor designs. It is desired that the biofuel and chemical building blocks commercialization via biomass pyrolysis can gradually reduce the global dependency on the non-renewable petroleum feedstocks as well as improving the country's waste management system.

1.5 Thesis organization

Chapter 1 elucidates the introduction which includes the research background, research objective, research scope and significance of the study.

Chapter 2 consists of a literature review which elaborates on the previous findings related to the influence of alkali and alkaline earth metals on biomass characterization, biomass thermal degradation, pyrolysis product yield, chemical compositions, kinetic and correlation analysis.

Chapter 3 provides experimental procedures such as biomass preparation and characterization, thermal degradation analysis, pyrolysis of palm kernel shell, characterization of pyrolysis oil, kinetic procedures and correlation analysis involved to evaluate the influence of AAEM on pyrolysis of palm kernel shell.

Chapter 4 discusses the results on the influence of AAEM based on the physicochemical properties, thermal degradation analysis, pyrolysis product yield chemical composition of pyrolysis oil, kinetic analysis and correlation study.

Finally, Chapter 5 concludes the findings and highlights the significance of this research. Besides, recommendations for future works on this research are suggested in this chapter.

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LIST OF PUBLICATION

Indexed Journal

1. **Zaman, K**., Balasundram, V., Ibrahim, N., Samsudin, M., Kasmani, R., Abd Hamid, M., & Hasbullah, H. (2018). Effect of Particle Size and Temperature on Pyrolysis of Palm Kernel Shell. International Journal of Engineering & Technology, 7(4.35), 118-124. doi:http://dx.doi.org/10.14419/ijet.v7i4.35.22339. **(Indexed by SCOPUS)**

Non-Indexed Conference Proceedings

1. **Zaman, K**., Ibrahim N, Dinie M, Samsudin M, Kasmani R, Supee A, et al. Thermal Degradation and Kinetic Analysis of Treated Palm Kernel Shell. In *8th International Graduate Conference on Engineering, Science and Humanities*. Johor Bahru; 2020. p. 9–12.