

**UNIVERSITI TEKNOLOGI MARA**

**ENHANCING AROMATIC  
HYDROCARBON THROUGH  
CATALYTIC PYROLYSIS ON  
SEQUENTIAL PRE-TREATMENT OF  
PALM EMPTY FRUIT BUNCH  
(PEFB)**

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**PhD**

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## AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the results of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

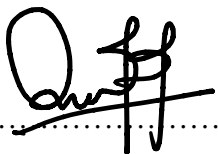
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## ABSTRACT

Bio-oil produce from untreated biomass through pyrolysis consists of undesirable oxygenated chemical compounds that contribute to the low quality of products. Introduction of sequential pre-treatment on biomass prior to pyrolysis shows a promising technique to enhance aromatic hydrocarbon in the bio-oil as an essential precursor for the synthesis of additive fuel, plastisizer and formation of polymeric compounds. In this study, the sequential pre-treatments of demineralization and torrefaction palm empty fruit bunch (PEFB) successfully carried out using a fixed-bed reactor in inert nitrogen gas at ambient pressure. The optimization on the pyrolysis process conditions was done using response surface methodology (RSM) using a central composite design (CCD) due to it was employed for the quadratic model that can estimate the individual second-order effect. Then, ANOVA was used to analyse the statistical parameters with the aid of RSM. HZSM-5 catalyst was used as a catalytic cracking catalyst during catalytic pyrolysis and reaction mechanism between HZSM-5 and torrefied demineralized palm empty fruit bunch (TDPEFB) was proposed based on the chemical compounds obtained in the bio-oil yield. Initially, demineralization was performed on PEFB by sonicating 1% nitric acid for 10 min to reduce the alkali and alkaline earth metals (AAEM). Torrefaction on the demineralized PEFB (DPEFB) was carried out to eliminate the undesirable components such as carboxyl, moisture and oxygen content using a fixed-bed reactor in inert nitrogen gas at 240 °C for 30 min. The sequential pre-treatment of TDPEFB at 240 °C showed the positive results with increased in carbon content to 49.34%, decreased in oxygen content at 44.78% and acceptable in ash content of 1.87% as compared to untreated PEFB with the amount of 44.97%, 47.25% and 4.21%, respectively. This verifies that the sequential pre-treatment enhance the characteristic of TDPEFB 240 prior to pyrolysis and catalytic pyrolysis processes. Pyrolysis on TDPEFB 240 at optimum conditions with reaction temperature of 490 °C ( $\pm 15$  °C) with heating rate of 85 °C $\cdot$ min<sup>-1</sup> for 4.16 min showed a slight increase in bio-oil yield up to 59.53% in comparison to 56.83% obtained from untreated PEFB. This observation explained that by the removal of AAEM through demineralization and reducing oxygen content through torrefaction in TDPEFB promotes the primary reactions that increase the bio-oil yield. It seemed that demineralization and torrefaction pre-treatment contribute to enhancement the quality of bio-oil yield by retarding secondary reaction and eliminating oxygen content through dehydration, dehydroxylation, decarbonylation and decarboxylation reactions. Further, the optimal conditions on catalytic pyrolysis of TDPEFB 240 for the maximum bio-oil yield of 59.20% were obtained at reaction temperature of 537 °C ( $\pm 15$  °C), holding time of 4.55 min and catalyst loading of 10%. Based on the GC-MS analysis, sequential pre-treatment of TDPEFB 240 on catalytic pyrolysis in the presence of HZSM-5 zeolite catalyst increased the formation of phenolic compounds (44.27%) and aromatic hydrocarbon compounds (9.35%), whereas reduction in organic acids and oxygenated compounds in the bio-oil were observed. From these results, catalytic pyrolysis of TDPEFB 240 revealed that there is significant effect on the sequential pre-treatment and HZSM-5 zeolite catalyst during the catalytic pyrolysis process. It can be described through possible proposed reaction mechanism of cracking catalyst with TDPEFB 240 that involve hydrocarbon pool and phenolic pool mechanisms towards the formation of aromatic hydrocarbon compounds based on the result from GC-MS analysis of bio-oil.

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