



UNIVERSITI PUTRA MALAYSIA

**MODIFIED DOLOMITE-BASED CATALYST FOR BIOFUEL
PRODUCTION VIA CATALYTIC PYROLYSIS OF WASTE COOKING
OIL**

RAJA MOHAMAD HAFRIZ BIN RAJA SHAHRUZZAMAN

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By

RAJA MOHAMAD HAFRIZ BIN RAJA SHAHRUZZAMAN

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirement for the Degree of Doctor of Philosophy**

January 2019

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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January 2019

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The limited availability of conventional energy resource, critical issues in food security and significant environmental problems have driven to seek renewable and sustainable resource of liquid fuel. In this respect, catalytic pyrolysis of waste cooking oil (WCO) represents a promising option for the future to produce value added biofuel. In this study, Malaysian Dolomite was successfully used as a base solid catalyst in converting WCO to green biofuel using lab-scale fractionated catalytic pyrolysis system.

The biofuel produced was in the range of gasoline, kerosene and diesel fraction with low acid value and low amount of aromatic hydrocarbon content as compared to biofuel produced by several commercial catalysts. Calcined Malaysian dolomite (CMD900) under flow of N₂ at 900°C produced catalyst with very high activity due to decomposition of CaMg(CO₃)₂ phase and formation of MgO-CaO phase. In addition, Malaysian dolomite showed high reactivity with 76.5% in total liquid hydrocarbon with 23.5% amount of oxygenated compound content in pyrolysis oil production.

In order to get a higher conversion of WCO and yield in pyrolysis oil production, Malaysian dolomite was modified with dispersion of various transition metals via different techniques of catalyst preparation. The modified Malaysian dolomite increased the surface area (12.02 m²/g to 18.22 m²/g) and lesser average pores diameters reduced (63.07 nm to 48.20 nm). In addition, modified Malaysian dolomite catalysts with dispersion of 5% Nickel via precipitation technique showed a high basicity properties with capability to desorb more CO₂. The conversion of WCO were totally improved from 36.0 wt% to 68.0 wt%, while the yield of pyrolysis oil increased from 13.4 wt % to 36.4 wt%. The pyrolysis oil produced using this catalyst showed high reactivity with 80.2% in total liquid hydrocarbon with only 19.8% oxygenated compound content.

The influence of the reaction variables such as the operating temperature, operating time, ratio catalyst to WCO and flow of nitrogen gas in biofuel production were optimized using RSM for maximum conversion of WCO as maximum yield of pyrolysis oil and yield of desired product (C₈-C₂₄). The results showed that optimum conditions for catalytic pyrolysis were at 410°C, 5.50 wt% catalyst loading, 60 min at 175 cm³/min nitrogen gas flow producing 92.0 wt% of conversion with 62.9 wt% yield of pyrolysis oil and 68.9% of desired product (C₈-C₂₄). The biofuel generated from catalytic cracking of WCO meets requirements of diesel and hydrocarbon biofuel standards for fuel application. Waste-to-wealth can be achieved using this cheaper technology due to waste cooking oil as feedstock, local carbonate mineral as catalyst and pyrolysis oil for potential biofuel is generated.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**PENGUBAHSUAIAN PEMANGKIN BERASASKAN DOLOMIT UNTUK
PENGHASILAN BIO-BAHAN BAKAR MELALUI PIROLISIS
PEMANGKINAN MINYAK MASAK TERBUANG**

Oleh

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Kewujudan sumber tenaga konvensional yang terhad, isu kritikal dalam keselamatan makanan dan masalah alam sekitar yang penting telah mendorong untuk mendapatkan sumber bahan bakar cecair yang boleh diperbaharui dan lestarian. Dalam hal ini, pirolisis pemangkin minyak masak terbuang mewakili pilihan yang menjanjikan masa depan untuk menghasilkan tambah nilai bio-bahan api. Dalam kajian ini, Dolomit Malaysia telah berjaya digunakan sebagai pemangkin pepejal asas dalam menukar minyak masak terbuang ke bio-bahan bakar hijau. Menggunakan sistem pirolisis pemangkin terpecah berskala makmal.

Bio-bahan bakar yang dihasilkan adalah dalam pelbagai pecahan seperti petrol, minyak tanah dan diesel dengan nilai keasidan yang lebih rendah dan kandungan hidrokarbon aromatik yang lebih rendah berbanding bahan bakar yang dihasilkan dengan penggunaan beberapa pemangkin komersil. Dolomit Malaysia (CMD900) yang diaktifkan di bawah aliran N_2 pada $900^\circ C$ menghasilkan aktiviti pemangkin yang sangat tinggi melalui penguraian fasa $CaMg(CO_3)_2$ dan pembentukan fasa $MgO-CaO$. Di samping itu, Dolomit Malaysia menunjukkan kereaktifan tinggi dengan penghasilan 76.5% jumlah hidrokarbon cecair dengan 23.5% jumlah kandungan sebatian teroksigen dalam pengeluaran minyak pirolisis.

Untuk mendapatkan penukaran minyak masak terbuang yang lebih tinggi dan penghasilan pengeluaran minyak pirolisis, Dolomit Malaysia telah diubahsuai dengan penyebaran pelbagai logam peralihan melalui penyediaan teknik pemangkin yang berbeza. Dolomit Malaysia yang diubahsuai telah meningkatkan kawasan permukaan ($12.02 \text{ m}^2/\text{g}$ hingga $18.22 \text{ m}^2/\text{g}$) dan menurunkan diameter purata liang (63.07 nm hingga 48.20 nm). Di samping itu, pemangkin Dolomit Malaysia yang telah diubahsuai dengan penyebaran 5% Nikel di bawah teknik pemendakan menunjukkan sifat asas alkali yang tinggi dengan keupayaan untuk menghilangkan lebih banyak CO_2 . Penukaran minyak masak terbuang telah meningkat sepenuhnya daripada 36.0% berat kepada 68.0% berat manakala hasil minyak pirolisis meningkat daripada 13.4% berat

kepada 36.4% berat. Minyak pirolisis yang dihasilkan menggunakan pemangkin ini menunjukkan kereaktifan yang tinggi dengan 80.2% dalam jumlah hidrokarbon cecair dengan hanya 19.8% jumlah kandungan sebatian teroksigen.

Pengaruh pembolehubah tindak balas seperti suhu operasi, masa operasi, nisbah pemangkin kepada minyak masak terbuang dan aliran gas nitrogen dalam pengeluaran bio-bahan bakar dioptimumkan menggunakan metodologi permukaan gerak balas (RSM) untuk penukaran maksimum minyak masak terbuang sebagai hasil maksimum minyak pirolisis dan hasil produk yang dikehendaki (C_8-C_{24}), masing-masing. Hasilnya menunjukkan bahawa keadaan optimum untuk pirolisis adalah pada $410^{\circ}C$, beban pemangkin sebanyak 5.50% berat dan 60 minit pada $175\text{ cm}^3/\text{min}$ aliran gas nitrogen menghasilkan 92.0% berat penukaran, 62.9% berat hasil pirolisis dan 68.9% produk yang dikehendaki (C_8-C_{24}). Bahan bakar yang dihasilkan daripada pirolisis pemangkin minyak masak terbuang memenuhi keperluan piawai diesel dan hidrokarbon untuk aplikasi bahan api. Sisa-kepada-kekayaan dapat dicapai dengan menggunakan teknologi murah ini kerana minyak masak terbuang sebagai bahan mentah, mineral karbonat tempatan sebagai pemangkin dan minyak pirolisis untuk bio-bahan bakar yang berpotensi dihasilkan.

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This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
ANOVA	Analysis of Variance
BET	Brunnauer-Emmett-Teller
CaO	Calcium Oxide
CaCO ₃	Calcium Carbonate
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
CMD900	Calcined Malaysian Dolomite (900°C)
DTG	Differential Thermal Gravimetric
EDX	Energy-Dispersive X-ray
EN	Euro Norm
FCC	Fluid Catalytic Cracking
FID	Flame Ionization Detection
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas Chromatography–Mass Spectrometry
H ₂ O	Water
MgO	Magnesium Oxide
MgCO ₃	Magnesium Carbonate
N ₂	Nitrogen Gas
NiO	Nickel Oxide
NMD	Natural Malaysian Dolomite
NO	Nitrogen Monoxide
RSM	Response Surface Methodology
SO ₂	Sulfur Dioxide
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analyzer
TG	Thermogravimetric Curve
TPD	Temperature Programmed Desorption
WCO	Waste Cooking Oil
XRF	X- Ray Fluorescence
XRD	X-Ray Diffraction
g	gram
h	hour
min	minute
ml	milliliter
mm	millimeter
nm	nanometer
rpm	rotation per minute
wt%	percent weight

CHAPTER 1

INTRODUCTION

1.1 Background

The challenges of skyrocketing fuel prices, environmental problems and dwindling reserve of conventional energy resources have increased the awareness to seek other potential sustainable resources for petroleum based fuel production. According to Wang *et al.*, 2017, the coal reserves will be diminished at 2112, and it will be the only fossil energy after 2042. The dependence of petroleum fuel in energy and transportation are commonly associated with the environmental impact of GHG emissions issue (Silva *et al.*, 2016). In the past decades, the influence of the shortage of petroleum reserves and public concerns on environmental issues have generated great interest in advancing the development of renewable energy (Wang *et al.*, 2017). The European Union has urged the utilization of biofuels in the transport sector through directives such as 2003/30/EC, 2009/28/EC and 2014/94/EU (Romero *et al.*, 2016). The use of biofuels can be used in current vehicles in any proportion without the need for modifications in the engines and infrastructures for storage (Souza *et al.*, 2018). Recently, biofuel has used as alternative to petroleum based fuel because of its biodegradability, renewability and fewer gas emissions.

Due to this current scenario, both edible oils such as palm, soybean, rapeseed and non-edible oils such as jatropha, karanja and rubber seed can be used as alternative feedstock in the biofuel production in particular biodiesel. However, the food security issues, limited edible oils availability and raw material cost are always critical issues in the biofuel production. Many studies have been conducted to find more efficient and cheaper biofuels from various non-edible and waste sources since these sources have been introduced as the second generation of raw materials for biofuel production (Busic *et al.*, 2018). Utilization of WCO has improved the efficiency in the use of waste materials and energy recovery process (Romero *et al.*, 2016). In recent years, there has been an increasing interest to study the potential of waste cooking oils (WCO) as a feedstock in biofuel production. Those waste oils, which usually just throw away, have the economic and environmental advantage compared to other alternative feedstocks. Cetinkaya *et al.* (2004), a similarity in the quality and yield of biofuel derived from WCO and from edible oil at optimum operating condition.

The biofuel produced from vegetable oils which contains primarily of triglycerides (90-98%) can be converted into high energy density liquid fuel. However, its application as transportation fuel is limited due to its viscous nature and poor low temperature properties. Problems such as incomplete combustion and solidification due to this nature require molecular structure modification of the vegetable oil. The modification via chemical reaction can be employed using several condition processes for example, esterification-transesterification process at mild temperature process and either thermal or catalytic cracking, hydrogen based process at high temperature.

Different process produces a different range of biofuel. For example, esterification-transesterification and thermal or catalytic cracking can be used to convert triglyceride to biofuel in the range of biodiesel and gasoline/kerosene/diesel, respectively.

Catalytic pyrolysis process offers several added advantages over esterification-transesterification including lower processing costs, flexibility of feedstock and compatibility with fuel standards, available engines and infrastructures (Xu *et al.*, 2010) and similar fuel quality from petroleum refining process. In addition, the catalytic pyrolysis process enables the selectivity of desired products. The esterification-transesterification process also generate biofuel in the range of biodiesel. However, the application of biodiesel as a high grade fuel reach its limitations due to oxidative stability and low specific energy content in presence of oxygen and cold flow properties (Maher and Bressler, 2007). In comparison to hydrocracking or hydrotreating, the processes are more expensive than catalytic cracking due to hydrogen needed during the processes. Furthermore, co-processing in hydrogen based units are the poisoning of catalyst by water coming from hydrodeoxygenation reactions and the low quality of the resulting hydrogenated product (mainly bad in cold properties). This requires additional process steps and cost.

Thermal cracking or pyrolysis of triglycerides involves the chemical decomposition caused by heat in oxygen-free environment to form smaller molecules. But, its interest in fuel transport application is reduced due to high amount of oxygen content is found in the pyrolysis oil. In contrast, catalytic pyrolysis is more selective and faster than thermal cracking which allows working at mild reaction condition and hence minimizing product yield towards coke, heavy fraction and gases and maximizing the liquid fraction production. Moreover, the presence of catalyst shows a great potential ability to remove the oxygen content and convert them into CO₂, CO, mixture of hydrocarbon and water. Solid acid catalysts such as HZMS-5, FCC and Y Zeolite are usually used as catalysts for the pyrolysis process due proper size pore and good shape selectivity. However, as reported by Wiggers *et al.*, (2009), the acid value of pyrolysis oils is more than 120 mg KOH/g due to the present of high carboxylic acid. This will be given a large effects on the corrosion value, cold filter plugging and freezing point of pyrolysis oil (Xu *et al.*, 2009, 2010).

Therefore, solid base catalyst is expected to obtain pyrolysis oils with good quality of biofuel in terms of good cold flow properties and low acid values. Dolomite (base catalyst) is a naturally abundant rock found in Malaysia and widely used in others process. At present, a major usage of dolomite is cement manufacturing due to its very low cost and non-toxic material. Chemically, dolomite mainly consists of calcium carbonate (CaCO₃) and magnesium carbonate (MgCO₃) with a small amount of impurities compounds. Similar to the others natural sources of calcite, CaCO₃, at high temperatures of calcination, the carbonate groups of dolomite decomposed to highly basic CaO and MgO. However, dolomite has received less attention in the basic catalyzed chemical syntheses, in spite of its high basicity, low cost catalyst, environmental friendliness and less toxicity (Ngamcharussrivichai *et al.*, 2007).

Therefore, this project is aimed to study heterogeneous catalyzed pyrolysis of waste cooking oil over various modified dolomites based catalyst in producing biofuel in the range of biogasoline, biokerosene and biodiesel. The studies on influences of variety of transition metals (active ingredients), calcinations of the parent dolomite, various operating parameters namely temperature, reaction time, flow of inert gas and catalyst to oil ratio need to be investigated. The synthesis of new modified based catalyst to produce an improved product suitable for biofuel (in the range of biogasoline, biokerosene and biodiesel) in accordance to standard fuel is expected to be developed.

1.2 Problem Statement

Cost of raw material and limited availability of edible oil due to food security are always critical issues for the biofuel production. Non-edible oil such as WCO is abundant in Malaysia and considered as an alternative and potential source for producing biofuel. As we know, the harmful disposal of WCO into drains give a bad environmental impact. The traditional reaction such as esterification/transterification reactions for synthesis of biofuel (diesel range) using a non-edible oil and acid base system has reached its saturation. The problem associated by using this traditional reaction involves a costly extraction procedure for glycerol recovery and formation of soap leads to decreasing liquid biofuel production. Besides that, the final product from these reaction contain high oxygen compound (less stable) which can cause serious damage to the engine filter, plug and corrode to the metals part of system process.

Catalytic pyrolysis method in decarboxylation applies mild thermal energy with appropriate catalyst to crack hydrocarbon compound, thus it is not necessary to carry out any stages for separating product or refining catalyst and decreasing soap formation. Catalysts applied in catalytic cracking process are usually solid catalysts such as zeolite catalyst and metal impregnated MCM41 which exhibit a high carboxylic acid compound in cracking oil (acid value more than 120 mg KOH/g). This undesirable product have a large effect on the corrosion value (lead to corrosion of the equipment), freezing point and cold filter plugging point of biofuel. To solve these unwanted effects, local cheap dolomite (carbonate derived catalyst) and transition metal can be used in catalytic cracking. Transition metal and their oxides have widely used to crack hydrocarbon due to dissociative chemisorption of organic materials on their surface. For example, NiO-loaded into calcined dolomite catalyst was reported an outstanding performance in gasification and transesterification (Kay *et. al.*, 2017 and Zhang *et. al.*, 2017).

Natural Malaysian dolomite or known as “Batu Reput” by the Malaysian people is abundantly found in northern part of Peninsular Malaysia, Perlis. Malaysian dolomite is the alkaline earth oxide and principally comprises of CaCO_3 and MgCO_3 with a small number of impurities such as ferrite and silica. Malaysian dolomite is very cheap and non-toxic material to be used as a catalyst in a few reaction process such as gasification and pyrolysis. Malaysia dolomite is magnesium ore and active only in the calcined form (CaO-MgO), whereby the transformation occurs around $>850^\circ\text{C}$ under atmospheric pressure. Due to the decomposition of carbonate groups, dolomite can act as a base catalyst and can be used in catalytic pyrolysis. Meanwhile, the usage of the

base catalyst resulted in less coke formation and leading to the occurrence of the undesirable cracking activity (Asikin Mijan *et. al.*, 2017).

Dolomite derived catalyst shows great thermal and mechanical robustness which can recycle use with little sign of performance decrease. However, dolomite is a base solid catalyst. Based on traditional base catalyst studies, it can decrease the acid values of biofuel produced from edible and non-edible oil, but the soap formation in the biofuel may be increased, which can lead to the decreasing of liquid biofuel production. Furthermore, in the gasification process, dolomite was rapidly deactivation due to carbon deposition and attrition as well as very brittle. Therefore, the need to improve the properties of the dolomite catalyst as a solid base catalyst is strongly needed. Nevertheless, there is limited knowledge of heterogeneous solid base catalyst used as a deoxygenation catalyst and dolomite catalyst still not yet to be tested in the catalytic pyrolysis or deoxygenation reaction (DO).

1.3 Objectives

The general objective of this research is to convert waste cooking oil into value-added product via catalytic pyrolysis. The specific objectives of this research are

1. To examine the suitability of Malaysian dolomite for use as a deoxygenation catalyst and the effects of the calcination process on dolomite's catalytic activity in the catalytic pyrolysis of waste cooking oil process.
2. To evaluate activities of dolomite based catalyst formulations using various active metal ingredients and catalyst preparation techniques.
3. To assess the optimum process parameters in the catalytic pyrolysis of WCO using selected dolomite based catalyst and physical and chemical properties as well as thermal stability of the biofuel.

1.4 Scope of work

The scopes of study are clearly defined to achieve the goal of this research and are listed as follows:

1. The suitability of Malaysian dolomite as catalyst is tested via catalytic pyrolysis of WCO and its performance is compared with the commercial catalysts. Catalytic pyrolysis of WCO is done by fractionated cracking system and the performance of Malaysian Dolomite as catalyst is enhanced through calcination process. The biofuels produced is characterized using Fourier Transform Infrared Absorption (FTIR) and Gas Chromatography- Mass Spectroscopy (GC-MS) for qualitative and quantitative analysis of pyrolysis oil.

2. The produced dolomite catalyst is formulated with different transition metals such as Fe, Co Ni, Cu and Zn to enhance its catalytic performance in the production of biofuel. Transition metals and their oxides have well known ability to crack hydrocarbon from triglycerides principally due to the dissociative chemisorption of organic materials on their surface. Different techniques preparation of catalyst such as Precipitation, Co-Precipitation and Incipient Wetness Impregnation technique are employed. The modified catalysts are distinguished, characterized and analyzed in terms of properties, morphology, basicity and activity of the catalysts.
3. The modified Malaysian dolomite catalyst with the best performance is selected and the statistical approach using Response Surface Methodology (RSM) is conducted for developing, improving and optimizing the catalytic pyrolysis of WCO. RSM is used in order to study the optimum reaction conditions for the catalytic pyrolysis of WCO using Malaysian Dolomite catalyst. The optimum process parameters are studied by considering various aspects of operating condition in order to determine the best quality and quantity of biofuel produce. In addition, various quality tests are carried out to assess the physical and chemical properties of the produced biofuel such as density, kinematic viscosity, flash point, cloud point, pour point, sulfur, carbon residue, cetane index, oxidation stability, acid value, iodine value & calorific value in comparison of biodiesel, diesel fuel and hydrocarbon fuel.

1.5 Thesis Outline

The thesis consists of nine chapters and the outline can be seen as follows.

Chapter 1 introduces the background studies, problem statement and the objectives of the research work in the field of biofuel production via catalytic cracking of WCO using Malaysian Dolomite as a catalyst. **Chapter 2** defines and analyzes the literature reviews on process overview, catalyst, technique preparation of catalyst and modification of Dolomite. Studies regarding catalyst and biofuel production from previous researchers are mentioned and presented in this chapter. **Chapter 3** explains the materials and methodology of the whole study. From the beginning of the development of catalyst such as preparation and characterization of catalysts to the product properties analysis, every step and approach is examined in details. **Chapter 4** presents the results and findings on preliminary studies of calcined Malaysian dolomite (CMD900) and commercial catalysts (ZSM-5, HY-Zeolite and FCC) using catalytic cracking of WCO. **Chapter 5** addresses the studies on modification of Malaysian dolomite with a dispersion of various transition metals namely nickel, zinc, copper, cobalt and iron in catalytic cracking of WCO. **Chapter 6** discuss the effects on different technique preparation of catalyst such as precipitation, co-precipitation and incipient wetness impregnation technique with the dispersion of nickel metal. **Chapter 7** describes the optimization of biofuel production from WCO via catalytic pyrolysis using Response Surface Methodology (RSM) and also conduct the analysis of product properties to assess the potential of WCO biofuel as an environmental friendly energy alternative. Finally, **Chapter 8** presents the conclusion of the research study and the recommendations for future work.

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LIST OF PUBLICATIONS

The articles that were published and submitted by the author during his PhD study are as follows:

Journal Publications:

Faten Hameed Kamil, A. Salmiaton, **Raja Mohamad Hafriz Raja Shahruzzaman**, R. Omar, Abdulkareem Ghassan Alsultan (2016). Characterization and Application of Aluminium Dross as Catalyst in Pyrolysis of Waste Cooking Oil. *Bulletin of Chemical Reaction Engineering & Catalysis*. 12 (1): 81-88.

Hafriz, R.S.R.M., Salmiaton, A., Yunus, R., Taufiq-Yap, Y.H. 2018. Green Biofuel Production via Catalytic Pyrolysis of Waste Cooking Oil using Malaysian Dolomite Catalyst. *Bulletin of Chemical Reaction Engineering & Catalysis*. 13 (3): 489-501

Proceedings Publication:

Raja Mohamad Hafriz Raja Shahruzzaman, Salmiaton Ali, Robiah Yunus, Taufiq-Yap Yun Hin. Modified Local Carbonate Mineral as Deoxygenated Catalyst for Biofuel Production via Catalytic Pyrolysis of Waste Cooking Oil. AIP Conference Proceedings 2030, 020006 (2018); <https://doi.org/10.1063/1.5066647>. *The 4th International Conference on Green Design and Manufacture 2018*.

Conferences:

1. The 4th International Conference on Green Design and Manufacture 2018 (IConGDM2018). 29-30 April 2018. Eden Star Saigon Hotel, Ho Chi Minh, Vietnam.
2. International Conference on Catalysis 2018 (Icat2018). 13-15 November 2018. Bangi-Putrajaya Hotel, Selangor, Malaysia.
3. 31st Symposium of Malaysian Chemical Engineers (SOMChe 2018). 5-6 December 2018. Hotel Istana, Kuala Lumpur, Malaysia.



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