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SYNTHESIS AND CHARACTERIZATION OF K_2O-DOLOMITE SOLID BASE CATALYSTS FOR METHYL ESTER PRODUCTION FROM PALM OIL

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By

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Biodiesel is one of the promising substitutes for petroleum-based diesel due to its numerous benefits. Generally, homogeneous catalysts are used in the methyl ester production, exhibiting better catalytic activity. However, this catalyst is associated with a number of shortcomings, these includes tedious in separation, generates a colossal amount of wastewater and difficult to recover. These economic and environmental drawbacks can be resolved with the help of heterogeneous catalysts, where they can be reused repeatedly without any major loss in their catalytic activity, making the process more economical and environmentally friendly. In this work, potassium oxide doped dolomite (K_2O-dolomite) catalysts were prepared by impregnation method with a loading of 5, 10, 15 and 20 wt% K_2O and labelled as 5 wt% K/D, 10 wt% K/D, 15 wt% K/D, and 20 wt% K/D, respectively. The catalysts were calcined in a static air at 850 °C for 3 hrs. X-ray diffraction (XRD) analysis of dolomite revealed the presence of calcium oxide (CaO) and magnesium oxide (MgO) phases with high crystallinity, in which intensity reduced after doped with varying concentrations of K_2O. Scanning electron microscope (SEM) revealed that as more K_2O was doped on dolomite, the particles became more agglomerated as opposed to a homogeneously small-sized particles on un-doped sample that lead to severe decrease of BET surface area from 19.0 m^2/g in dolomite to 1.3 m^2/g in 20 wt% K/D. However, the high activity of the doped catalyst was dictated by the high amount of basic site, as evidenced in Temperature Programmed Desorption of carbon dioxide (TPD-CO_2) which showed an increase in the capacity of the basic site with an increased amount of K_2O as in the case of 15 wt% K/D. Thermo Gravimetry–Differential Thermal Gravimetry analysis (TG-DTG) of all the samples showed a similar onset degradation temperatures with three decomposition signals. Fourier Transmission infrared spectroscopy (FT-IR) confirmed the presence of CaO and MgO which corroborated well with XRD results. The transesterification reaction was optimized by Taguchi method involving four levels and five factors (reaction temperature, reaction time, methanol to oil molar ratio, catalyst amount and K_2O loading). The results indicated that temperature is the most significant parameter influencing the methyl ester yield, followed by methanol to oil molar ratio, catalyst amount and K_2O loading while reaction time was not a significant factor. The optimum

conditions observed for maximum methyl ester yield of 98.7% were temperature 60 °C, methanol to oil molar ratio 12:1, catalyst amount 1 wt.%, K_2O loading 15 wt.% and reaction time 1h. The 15 wt% K/D catalyst displayed the best catalytic performance due to its highest total basicity content. The physicochemical properties of the produced methyl ester were found to conform with the ASTM D6752 and EN1421 specification. The catalyst can still possess a rather high methyl ester yield after reused for 6 cycles with a negligible decrease in activity due to K^+ ions leached into the product. Overall, doping of K_2O in the catalyst has significantly improved the catalytic activity in the transesterification of palm oil.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysis sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS DAN PENCIRIAN MANGKIN PEPEJAL BES K_2O-DOLOMIT UNTUK PENGHASILAN METIL ESTER DARIPADA MINYAK SAWIT

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Biodiesel merupakan suatu pengganti pilihan kepada diesel berasaskan petroleum disebabkan oleh kepelbagaian faedahnya. Umumnya, mangkin homogen digunakan secara meluas di dalam penghasilan biodiesel, namun begitu proses ini mempunyai banyak kelemahan seperti pemisahan yang sukar, penghasilan air sisa berlebihan dan kesukaran untuk memperolehi semula mangkin. Kelemahan ekonomi dan persekitaran ini boleh diatasi dengan bantuan mangkin heterogen, di mana ianya boleh digunakan berulang kali tanpa kehilangan besar aktiviti pemangkinan yang menjadikan proses lebih ekonomi dan mesra alam sekitar. Di dalam kajian ini, mangkin kalium terdop dolomit (K_2O-dolomit) telah disediakan menggunakan kaedah impregnasi dengan muatan 5 , 10, 15, dan 20 wt% K_2O dan dilabel masing-masing sebagai 5 wt% K/D, 10 wt% K/D, 15 wt% K/D, dan 20 wt% K/D. Mangkin tersebut telah di kalsinasi dalam udara statik pada 850 °C selama 3 j. Pembelauan sinar-X (XRD) terhadap dolomit menunjukkan kehadiran fasa kalsium oksida (CaO) dan magnesium oksida (MgO) dengan penghabluran tinggi, yang mana intensiti fasa-fasa tersebut didapati berkurangan selepas didop dengan pelbagai kepekatan K_2O. Mikroskopi elektron pengimbasan (SEM) menunjukkan semakin banyak K_2O didop pada dolomit, partikel menjadi semakin aglomerat sebaliknya dolomit tidak didop menunjukkan partikel bersaiz kecil yang seterusnya membawa kepada penurunan teruk luas permukaan Brunauer–Emmett–Teller (BET) dari 19.0 m^2/g pada dolomit ke 1.3 m^2/g pada 20 wt%K/D. Walaubagaimanapun, aktiviti tinggi yang ditunjukkan oleh mangkin terdop ditentukan oleh kandungan tapak bes yang tinggi, sebagaimana dibuktikan oleh program nyahjerapan suhu karbon dioksida (TPD-CO_2) yang menunjukkan peningkatan kapasiti tapak bes apabila muatan K_2O meningkat seperti yang dibuktikan oleh 15 wt%K/D. Analisis gravimetri terma-pembezaan gravimetri terma (TG-DTG) pada semua sampel menunjukkan suhu kemerosotan awalan serupa dengan tiga isyarat penguraian. Spektroskopi infra-merah transmisi Fourier (FT-IR) mengesahkan kehadiran CaO dan MgO yang memperkuatkan keputusan XRD. Tindak balas transesterifikasi telah dioptimumkan menggunakan kaedah Taguchi melibatkan empat aras dan lima faktor (suhu tindak balas, masa tindak balas, nisbah mol methanol kepada minyak, amaun mangkin dan muatan K_2O). Keputusan kajian menunjukkan suhu adalah parameter paling bererti mempengaruhi hasil metil ester,

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diikuti oleh nisbah mol metanol kepada minyak, amaun mangkin, dan muatan K_2O manakala masa tindak balas bukan faktor bererti. Keadaan optimum yang diperhatikan untuk hasil maksimum metil ester sebanyak 98.7% adalah suhu 60 °C, nisbah mol metanol kepada minyak 12:1, amaun mangkin 1 wt.%, muatan K_2O 15 wt.% dan masa tindak balas 1j. Mangkin 15wt%K/D menunjukkan prestasi pemangkinan paling terbaik kerana ia mengandungi jumlah kebesan paling tinggi. Sifat fizikal-kimia metil ester yang dihasilkan di dapati memenuhi spesifikasi ASTM D6752 and EN1421. Kajian kebolehgunaan mendapati mangkin 15wt%K/D masih menunjukkan hasil tinggi metil ester walaupun setelah 6 kitaran tindak balas dengan pengurangan aktiviti boleh diabaikan disebabkan pelarutlesapan ion K^+. Secara keseluruhannya, muatan K_2O pada mangkin di dapati memberi peningkatan ketara pada aktiviti pemangkinan di dalam transesterifikasi minyak sawit.

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

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LIST OF ABBREVIATIONS

TAG	Triglyceride
MAG	Monoglyceride
DAG	Diglyceride
FFA	Free fatty acid
FAME	Fatty acid methyl ester
S/N	Signal to noise ratio
DoE	Design of experiment
OA	Orthogonal Array
JCPDS	Join Committee on Powder Diffraction Standard
T_{max}	Temperature at maximum peak
XRD	X-ray diffraction`
TPD	Temperature programmed desorption
FT-IR	Fourier Transmission infrared spectroscopy
^{1}H-NMR	Proton Nuclear magnetic resonance
TGA	Thermogravimetry analysis
SEM	Scanning Electron Microscope
CD	Calcined dolomite

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Energy is a primary need for human to survive, owing to an incessant increase in the human population. The world's total energy is predominantly used in industry, transportation and power sector (Avhad and Marchetti, 2015). Most of the energy required is mainly from conventional sources of fossil fuels. These fossil fuels are formed as a result of organic matter buried beneath the earth for geological years in an anoxic condition, hence, producing a significant proportion of carbon such as coal, oil (petroleum) and gas (natural gas).

The use of these carbon-based fuels have several environmental issues, especially the release of high greenhouse gases, global warming and acid rain (Lit *et al.,* 2019). Furthermore, severe environmental concern, decrease in oil reserves, fluctuation of fuel price and excessive utilization of diesel fuel, particularly in the transportation sector, have triggered the search for a substitute to petro-diesel that are obtained from renewable sources, environmentally friendly, sustainable and less expensive (Singh *et al.,* 2020).

Biodiesel is a renewable source of fuel that is recognized as a better alternative to carbon based fuels because of its renowned benefits, which includes; biodegradability, sustainability, better engine efficiency, better combustion due to oxygen content, little or no engine modification, low level of toxicity and reduced greenhouse gas emission (Jamil *et al.,* 2020). Moreover, biodiesel can be blend with carbon based-diesel in all percentages. In most of the developed countries, they have been using the blended biodiesel with petro-diesel instead of 100 % biodiesel, almost always, blended petro-diesel is abbreviated by alphanumeric (B20, B40, B80) (Knothe and Gerpen, 2005; Lapuerta *et al.,* 2020).

Conventionally, biodiesel is produced via a reaction of triglyceride of vegetable oil or animal fats with low chain alcohol, preferably methanol in the presence of catalyst (acid or base) through a process known as transesterification reaction (Qu *et al.,* 2021). Though, it was revealed that the transesterification reaction using a basic homogeneous catalyst is 4000 times faster than acid homogeneous catalyst (Marques *et al.,* 2015). Nonetheless, the reaction exhibited a number of weaknesses which include difficult to recover, produced methyl ester must be neutralized and separated from the catalyst after the reaction, with subsequent generation of a colossal amount of wastewater (Baskar and Aiswarya, 2016; Guan-yi Chen *et al.,* 2016).

To circumvent the problems associated with the use of homogeneous catalysts, researchers have suggested the use of heterogeneous catalysts (Bambase *et al*., 2020). Some benefits of heterogeneous catalyst over a homogeneous catalyst are reported

somewhere else and these include easy separation, regenerability, reusability and negligible toxicity (Kataria *et al.,* 2018). Many heterogeneous catalysts have been used for the production of biodiesel. For example, a metal single-base oxide such as calcium oxide (CaO), magnesium oxide (MgO) and strontium oxide (Avhad and Marchetti, 2015).

Furthermore, the heterogeneous base catalyst is further categorized into solid alkali catalyst and base catalyst support. The catalyst exhibits a low catalytic activity per unit mass because the surface area is the only contact area between the triglyceride substrate and the catalyst. After introducing the active ingredient on the parent material with a large surface area, this served as an alternative source in reducing the amount of catalyst needed to get a similar level of catalytic activity (Chanatip *et al,* 2010). However, the catalyst support is also used to reduce the mass transfer limitation for solid catalyst during the transesterification reaction (Zabeti *et al,* 2009).

To date, only a small number among them (catalyst) are employed on a large scale as a result of catalyst processing costs. To overcome these drawbacks, a number researchers concentrated on natural sources or solid waste as materials for catalyst preparation. Clays from natural source materials such as bentonite (Boz *et al.,* 2013), hydrotalcite (Sun *et al.,* 2014), palygorskite (Shan *et al.,* 2016), and sepiolite (Aslan *et al.,* 2018), are found in excess. Their availability, inexpensive and environmentally friendly nature qualified them to be used as catalyst for biodiesel production.

Dolomite is one of the catalysts used in biodiesel production which is available and inexpensive with negligible toxicity. It occurs naturally with high basic strength and a reasonable surface area (Jindapon and Ngamcharussrivichai, 2018; Nur *et al.,* 2012). A number of basic salts have been widely used in solid catalyst, potassium salt such as K_2CO_3 has improve basic capacity significantly. Moreover, potassium salt also enhanced the catalytic activity in the transesterification reaction.

In this research, the basic capacity of dolomite was improved significantly by impregnating with potassium oxide (K_2O) and was used in the production of methyl ester under mild reaction condition. Furthermore, the influence of various reaction conditions (reaction temperature, reaction time, methanol to oil molar ratio, catalyst amount and K_2O loading) on methyl ester were investigated. The catalytic stability was investigated to evaluate the reusability and lixiviate of the catalyst.

1.2 Problem statement

Today, biodiesel production industry has been established in many countries, owing to its numerous benefits over the conventional diesel fuel. Conventionally, biodiesel is produced via transesterification of vegetable oil and animal fat with alcohol in the presence of homogeneous catalyst. However, homogeneous catalyst has numerous shortcomings, these include non-reusable, difficult in separation from the product and generation of colossal amount of wastewater. Therefore, these shortcomings have

stimulated search in the area of heterogeneous catalysts, where they can be reused repeatedly with negligible loss in their catalytic activity, making the process more economical and environmentally benign. Under this consideration, K_2O-dolomite is a heterogeneous base catalyst that is accessible, inexpensive, possess high basicity, negligible toxicity, and minimal side reaction and produced high methyl ester yield under mild reaction condition. Shan et al., (2016) investigated the catalytic activity of K_2CO_3/Polygorskite for transesterification of palm oil to biodiesel. 97.0% of methyl ester was attained under reaction condition of reaction temperature 60 ºC, reaction time 3.5h, catalyst amount 5 wt%, methanol to oil molar ratio 12:1, and K_2CO_3 loading 40 wt%. The maximum biodiesel yield attained was as a result of highest basicity. The catalyst could be reused up to 8 cycles with negligible decreased in the methyl ester yield (80 %). For optimization process, factors such as product of the process and the cost of production were established as limitation. A number of optimization process have been developed, however, vast majority of these process needs maximum number of runs which is cost, time and energy intensive. Another shortcoming of most of the process is that they are unable to provide information on the influence of each factor on the process. Consequently, the optimization process that can overcome these weaknesses was choose in this research to optimize the process parameters for the production of methyl ester. The reusability of the catalyst was evaluated to ascertained the stability of the synthesized catalyst

1.3 Research objectives

Objectives of the study;

i. To synthesize K_2O-dolomite using impregnation method and characterized using XRD, BET, SEM, TGA, FTIR and TPD-CO_2.
ii. To optimize the operating conditions using Taguchi method.
iii. To investigate the catalytic activity of the synthesized catalyst for the production of methyl ester from palm oil and to carry out the reusability study and leaching test.

1.4 Scope of research

The scope of this study involves synthesis of K_2O-dolomite by impregnation method. The synthesized catalyst was characterized to investigate the physicochemical properties using XRD, TGA, SEM, TPD-CO_2, BET and FTIR. The operating conditions (temperature, time, methanol to oil molar ratio, catalyst amount and K_2O loading) were optimized using Taguchi method. Reusability study was carried out using the optimum K_2O loading and to investigate the leaching of K^+ into the product.

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