ESTERIFICATION OF PALM FATTY ACID DISTILLATE USING SULFATE BASED CATALYSTS

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SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Science.

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citation which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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ABSTRAK

Kajian tentang biodiesel adalah penting sebagai penyelesaian masalah kekurangan bahan api fosil dan peningkatan pencemaran alam. Kajian ini memfokuskan penghasilan biodiesel dari proses esterifikasi sulingan asid lemak sawit (PFAD) menggunakan asid sulfurik dan tiga jenis mangkin heterogen iaitu SO_4^{2-}/Fe_2O_3, SO_4^{2-}/Al_2O_3 and SO_4^{2-}/DSBC (DSBC adalah tanah liat peluntur terpakai yang telah dinyah minyak). PFAD merupakan produk sampingan dari kilang sawit, mempunyai kandungan asid lemak bebas yang tinggi. Ujian pencirian menunjukkan PFAD yang digunakan dalam kajian ini mempunyai nilai asid 164.52 mgKOH/g, nilai iodin 52.3 g I_2/100g dan kandungan lembapan 0.26%. Kesemua mangkin heterogen dihasilkan melalui kaedah impregnasi basah menggunakan asid sulfurik dengan kaedah ultrasonik. Kaedah ultrasonik dipilih kerana telah terbukti membantu dalam penyediaan mangkin yang lebih cekap dibandingkan dengan penyediaan tradisional. Kesemua mangkin dicirikan dengan FESEM-EDX, XRD, FTIR, indikator Hammett, TGA dan BET. Kesemua mangkin mempunyai keasidan dalam julat $1.8<pH<3.0$. Antara semua mangkin yang dihasilkan, luas permukaan dan isipadu liang paling tinggi dimiliki oleh SO_4^{2-}/DSBC. Metil ester paling tinggi dihasilkan dengan mangkin heterogen SO_4^{2-}/Fe_2O_3 dengan 87.81% kandungan metil ester pada suhu 90 °C, 5 jam, 12:1 nisbah molar metanol kepada PFAD dan 7 wt% kandungan mangkin. Walaupun mangkin mengalami larut lesap, kebolehgunaan semula mangkin mencatatkan 76.02% pada kitaran keempat. Bagi SO_4^{2-}/DSBC pula, kandungan metil ester tertinggi didapati sebanyak 74.55% (pada 110 °C, 9 jam, 12:1 nisbah molar metanol kepada PFAD dan 5 wt% kandungan mangkin), dengan kitaran keempat guna semula mangkin mencatatkan 55.43%, manakala SO_4^{2-}/Al_2O_3 pula menghasilkan 67.81% metil ester (pada 110 °C, 9 jam, 12:1 nisbah molar metanol kepada PFAD dan 7 wt% kandungan mangkin).

ABSTRACT

Research on biodiesel is worth to be explored persistently as a promising solution for depletion of fossil fuel and to counter the escalation of environmental disruptions. This study focuses on the production of biodiesel by esterification of palm fatty acid distillate (PFAD) using sulfuric acid and three types of sulfated metal oxides, SO_4^{2-}/Fe_2O_3, SO_4^{2-}/Al_2O_3 and sulfated deoiled spent bleaching clay (SO_4^{2-}/DSBC). PFAD is by-product from palm oil refinery, containing high amount of free fatty acid. Characterisation test found that PFAD used in this study had acid value of 164.52 mgKOH/g, saponification value of 167.4 mgKOH/g, iodine value of 52.3 g I_2/100g and moisture content of 0.26%. All three solid catalysts were prepared by wet impregnation using sulfuric acid via ultrasonic method. Ultrasonic method is chosen as it had been proven to aid in catalyst preparation and produce better performing catalyst compared to the conventional preparation. All the catalysts were characterised using FESEM-EDX, XRD, FTIR, Hammett indicators, TGA and BET. All the catalysts have acidity in the range of $1.8<pH<3.0$. Among the catalysts, highest pore volume and surface area was recorded by SO_4^{2-}/DSBC. Highest conversion obtained from among the heterogenous catalyst was SO_4^{2-}/Fe_2O_3 with 87.81% methyl ester content at 90 °C, 5 h, 12:1 methanol to PFAD molar ratio and 7 wt% catalyst amount. Even with catalyst leaching, a conversion of 76.02% is achieved at fourth cycle of reusability. As for SO_4^{2-}/DSBC, highest methyl ester obtained was 74.55% (at 110°C, 5 h, 12:1 methanol to PFAD molar ratio and 5 wt% catalyst amount) with fourth reusability gave 55.43% conversion, while SO_4^{2-}/Al_2O_3 produced 67.81% methyl ester (at 110 °C, 9 h, 12:1 methanol to PFAD molar ratio and 7 wt% catalyst amount).

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATION

BET	Brunauer - Emmett – Teller
CCD	Central composite design
CCO	Crude coconut oil
CSTR	Continuous stirred tank reactor
CPKO	Crude palm kernel oil
CPO	Crude palm oil
DSBC	Deoiled spent bleaching clay
DSBC 700	Deoiled spent bleaching clay heat treated at 700 °C
FA	Fatty acid
FAME	Fatty acid methyl ester
FESEM	Field emission scanning electron microscopy
FFA	Free fatty acid
FTIR	Fourier transform infrared
GC-FID	Gas chromatography - flame ionization detector
PFAD	Palm fatty acid distillate
RSM	Response surface methodology
SBC	Spent bleaching clay
SDS 2M	Sulfated DSBC prepared using 2 M sulfuric acid
SDS 5M	Sulfated DSBC prepared using 5 M sulfuric acid
SFO 250	SO_4^{2-}/Fe_2O_3 calcined at 250 °C
SFO 400	SO_4^{2-}/Fe_2O_3 calcined at 400 °C
SFO 550	SO_4^{2-}/Fe_2O_3 calcined at 550 °C
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TLC-FID	Thin layer chromatography – flame ionization detector
XRD	X-ray diffraction

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