SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF SUPPORTED SUGAR CATALYSTS

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THESIS SUBMITTED IN FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ENGINEERING

**FACULTY OF ENGINEERING
UNIVERSITI MALAYSIA SABAH
2017**

UNIVERSITI MALAYSIA SABAH

BORANG PENGESAHAN STATUS TESIS

JUDUL: **SYNTHESIS, CHARACTERIZATIONS, AND CATALYTIC ACTIVITY OF SUPPORTED SUGAR CATALYSTS**

IJAZAH: **MASTER OF ENGINEERING (CHEMICAL ENGINEERING)**

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ACKNOWLEDGEMENT

First of all, I want to express my highest gratitude to The Almighty Allah s.w.t that without rezq He had given to me, I would not be able to complete this thesis. Second, to my supervisor Dr Jidon Adrian Janaun, for all the guidance, tolerance when my works were not as expected and whenever I missed the weekly meetings. Thank you for all the constructive comments on my works which I believe, you might waste a lot of precious time reading it. During my journey too, I never shortage of money or any other necessities because I was financially supported by Dr.Jidon and Dr. Nancy. Thank you to both of you for being concern, supportive and understanding supervisors. Next, I dedicated my appreciation to my parents, Mr Safie and Mrs Fodhilah, as well as my brothers and sisters that supported me morally and financially throughout my studies. To my husband Mohd Izuan Bin Mahmuda for being there all the time and to all your supports too, you are my strength and the reason I hold on. To my research mates, Poyo, Ola, Valey, Veron, and Winnie, you guys have made my journey so much fun and resourceful I could not forget our memories and moments together. To my beloved friends, Monjia Belleza Mojulat Cosmas, who helped me a lot, day and night, I pray for smoothness of your studies and happiness. Thank you everyone, I could not have done this without all of you, thank you.

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11 July 2017

ABSTRACT

The process of synthesizing sugar catalyst is started by incomplete carbonization of D-glucose. It is followed by sulphonation to incorporate the sulphonic group ($-SO_3H$). However, despite of its excellence catalytic performance, the current form of sugar catalyst is in powder form with non-porous structure maybe lack of applicability in commercial scale biodiesel production due to the potential of large pressure drop in a packed bed reactor. Hence, it is anticipated that the industrial applicability of sugar catalyst can be enhanced if its particle size can be increased. This study was conducted to investigate the feasibility of attaching sugar catalyst on different surfaces by depositing the char on external surfaces of aluminum (SCDCAl), glass (SCDCSi) and clay (SCDCCl) via dip coating method (*ex-situ*) followed by sulphonation. The sulfonation of char embedded naturally in different types of supports namely, rice husk, rice straw, and rice husk were also studied (*in-situ*). Rice husk and rice straw were pyrolyzed in a controlled condition, whereas rice husk ash, a combustion waste, was acquired from a local paddy mill. Synthesized supported sugar catalysts via *ex-situ* were sulphonated using fuming sulphuric acid via vapor-phase sulphonation and supported catalysts via *in-situ* were sulphonated via liquid phase sulphonation. The ratio of char deposited on SCDCAl, SCDCSi and SCDCCl were 0.900 g_c/g_s, 0.040 g_c/g_s, and 0.014 g_c/g_s, respectively. The total acidity for SCDCAl, SCDCSi, and SCDCCl were 0.9 mmol/g, 0.2 mmol/g, and 0.4 mmol/g, respectively. SCDCAl and SCDCGl had surface area of 3.38 m^2/g and 1.2 m^2/g, respectively compared to powder sugar catalyst which has less than <1 m^2/g. The catalysts were stable up to 673.15 K. Meanwhile, the total acidity of *in-situ* sulfonation of rice straw (RSC), rice husk (RHC) and rice husk ash (RHAC) were 3.60 mmol/g, 3.53 mmol/g and 2.28 mmol/g, respectively. FTIR data indicated the presence of silica bonded to carbon in the samples. The supported catalysts via *in-situ* undergone two stages of weight loss from T = 303.15 K to 673.15 K. The catalytic activity of SCDCAl was tested in a packed bed reactor and conversion of oleic acid was below than 1%. The catalytic activity of RSC, RHC and RHAC on esterification of oleic acid with methanol were studied in a batch reactor at 333.15 K, 343.15 K, and 353.15 K under reflux, molar ratio (oleic acid: methanol) of 1:10, 3 wt.% catalyst. The conversion of oleic acid using RHC and RHAC were linearly proportional to temperature. RSC had the highest oleic acid conversion compared to RHC and RHAC. Ea for esterification reaction catalyzed by RSC, RHC and RHAC were 25.952 $Kj.mol^{-1}$, 38.760 $Kj.mol^{-1}$ and 10.842 $Kj.mol^{-1}$ respectively. The kinetic model was studied using the integral method. Based on the regression of best fit line, RSC, RHC and RHAC followed second order reaction. In conclusion, sugar catalyst can barely be deposited externally on aluminum, clay and glass via *ex-situ* process with weak adhesion strength. Meanwhile, the sulfonated carbon-silica catalyst prepared via *in-situ* had high total acidity that likely due to the presence of carbon-silica bond. It had shown high catalytic activity on esterification of oleic acid with methanol.

ABSTRAK

SINTESIS, PENCIRIAN DAN AKTIVITI PEMANGKINAN SUGAR CATALYST YANG DISOKONG

Proses penghasilan sugar catalyst *dimulakan dengan proses pirolisis. Diikuti dengan sulfonasi* bagi penggabungan dengan kumpulan asid sulfonik (SO_3H). Bentuk *sugar catalyst* dalam serbuk adalah tidak poros dan kurang sesuai untuk dikormesialkan kerana potensi untuk menghasilkan penurunan tekanan di dalam *packed bed reactor*. Hal ini disebabkan oleh *packed bed* yang dimampatkan dengan pemangkin yang tidak poros dan luas permukaan yang rendah memerlukan lebih tenaga untuk mengatasi penurunan tekanan tersebut. Penurunan tekanan boleh mempengaruhi penghasilan biodiesel untuk tindakbalas dalam bentuk gas. Penyesuaian penggunaan *sugar catalyst* di dalam skala pengindustrian boleh dilakukan dengan pembesaran saiz partikel *sugar catalyst*. Kajian ini telah dijalankan untuk mengkaji kebolehan melekatkan *sugar catalyst* pada permukaan sokongan seperti aluminum (SCDCAl), gelas (SCDCGl) dan tanah liat (SCDCCl) secara berasingan melalui kaedah *dip-coating* (*ex-situ*) atau campuran sokongan secara semulajadi (*in-situ*) diikuti dengan proses sulfonasi untuk menghasilkan pemangkin yang disokong bersifat asid. Sekam padi, jerami padi dan abu sekam padi digunakan sebagai sampel untuk penggabungan pemangkin *sugar catalyst* dengan viethan melalui *in-situ proses*. Nisbah karbon yang terdapat pada SCDCAl, SCDCGl dan SCDCCl adalah 0.9 g_c/g_s, 0.040 g_c/g_s, dan 0.014 g_c/g_s. Jumlah keasidan SCDCAl, SCDCGl dan SCDCCl adalah 0.9 mmol/g, 0.2 mmol/g, dan 0.4 mmol/g. SCDCAl and SCDCGl mempunyai luas permukaan 3.38 m^2/g and 1.2 m^2/g berbanding dengan sugar catalyst bentuk serbuk yang mempunyai luas permukaan kurang dari 1 m^2/g. Kajian selanjutnya yang dijalankan menunjukkan SCDCAl, SCDCGl dan SCDCCl viethan terhakis akibat daripada impak mekanikal semasa digunakan untuk ujian pengasilan viethanolvi. Jumlah keasidan sulfonasi *in-situ* jerami padi (RSC), sekam padi (RHC) dan abu sekam padi (RHAC) adalah 3.60 mmol/g, 3.53 mmol/g dan 2.28 mmol/g. Data dari FTIR juga menunjukkan kewujudan hubungan viethan-karbon dalam RSC, RHC dan RHAC. Pemangkin yang disokong melalui *in-situ* melalui dua peringkat kehilangan berat dari suhu 303.15 K hingga 673.15 K. Aktiviti pemangkin disokong y dihasilkan melalui *ex-situ* atas aluminum (SCDCAl) telah diuji dalam reaktor *packed bed* dan menghasilkan konversi asid oleik kurang dari 1%. Manakala RSC, RHC dan RHAC telah diuji dalam reaktor *batch* pada tiga suhu berbeza iaitu 333.15 K, 343.15 K, and 353.15 K di bawah refluks, nisbah ratio asid oleik : methanol (1:10) dan 3.wt % berat pemangkin. Tindakbalas esterifikasi menggunakan RSC adalah yang tertinggi berbanding RHC dan RHAC. Model ethanol ditentukan menggunakan *integral method*. *Activation energy*, E_a untuk reaksi esterifikasi menggunakan RSC, RHC dan RHAC adalah 25.952 $Kj.mol^{-1}$, 38.760 $Kj.mol^{-1}$ and 10.842 $Kj.mol^{-1}$. Reaksi esterfikasi menggunakan RSC, RHC dan RHAC mengikut *order* 2. Secara keseluruhannya, *sugar catalyst* yang dihasilkan melalui proses *ex-situ* menunjukkan lekatan yang lemah pada permukaan sokongan aluminum, gelas dan tanah liat. Manakala pemangkin karbon-silika yang dihasilkan melalui *in-situ* mempunyai jumlah keasidan tinggi yang berkemungkinan disebabkan kewujudan karbon-silika dan telah menunjukkan fungsi pemangkinan yang lebih tinggi dalam tindak balas pengeksterifikasi asid oleik dan ethanol.

LIST OF CONTENT

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

K - Kelvin

k - Rate constant

$\propto$ - Order of reaction

A - Preexponential factor of frequency factor

E - Activation energy, J/mol or cal/mol Activation energy, J/mol or cal/mol

R - Gas constant = 8.314 J/mol. K = 1.987 cal/mol.K

$C_{OA\,.0}$ - Initial concentration of oleic acid at t = 0

C_{OA} - Concentration of oleic acid at time, t

LIST OF ABBREVIATIONS

FFA	-	Free Fatty Acids
TGs	-	Triglycerides
C_{oA}	-	Concentration of Oleic Acid (mol.dm^{-3})
COOH	-	Carboxyl groups
OH	-	Hydroxyl groups
SO_3H	-	Sulphonic groups
$C_{19}H_{36}O_2$	-	Methyl oleate
$C_{18}H_{34}O_2$	-	Oleic acid
CH_3OH	-	Methanol
BDL	-	Below Detection Limit
d.a.f	-	dry ash free
g_c/g_s	-	gram of char/gram of support
SCDCAl	-	supported sugar catalyst by dip coating method on aluminum
SCDCGl	-	supported sugar catalyst by dip coating method on glass
SCDCCl	-	supported sugar catalyst by dip coating method on clay
RHAC	-	Rice husk ash catalyst

RHC - Rice husk catalyst

RSC - Rice straw catalyst

LIST OF APPENDICES