ACIDS AND DEEP EUTECTIC SOLVENTS AS NOVEL CATALYSTS FOR THE PROCESSING OF LOW GRADE PALM OIL FOR BIOFUEL PRODUCTION

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ABSTRACT

This study introduces three new raw materials for biodiesel production, namely acidic crude palm oil (ACPO), low-grade crude palm oil (LGCPO) and mixed industrial palm oil (MIPO). MIPO which is a mixture of low-grade industrial oils, such as ACPO mixed with sludge palm oil (SPO). These raw materials can be characterized in terms of their fatty acid composition and physical properties. They have a similar content of saturated and unsaturated fatty acids. The molecular weight range of raw materials based palm oil is 816-836 (g/mol). Characterization of the abovementioned raw materials showed that they are non-edible and they can be considered as low-grade oils. A pre-treatment process is necessary to convert the free fatty acid (FFA) into fatty acid methyl ester before proceeding with biodiesel production. The development of a catalyst can be considered as a major contribution in the pre-treatment for biodiesel processing. Different types of acids were screened and the following homogenous acids were selected for further optimization: ethanesulfonic acid, methanesulfonic acid, trifluoromethanesulfonic acid, benzenesulfonic acid, (1R)-(-)-camphor-10-sulfonic acid, 1-propanesulfonic acid and chromosulfuric acid. The optimum conditions for all catalysts are approximately the same in terms of methanol loading, reaction temperature and reaction time, except for the catalyst dosage. Stronger acids require dosages ranging from 0.75%wt (catalyst to oil) to 1% while weaker organic acids need double the dosages to reduce the FFA content to acceptable level. Acids with fluorine atoms, such as trifluoromethanesulfonic acid are not recommended to be used in the biodiesel industry due to safety issues as well as unwanted reactions with air. As, under normal conditions, benzenesulfonic acid is in solid form and (1R)-(-)-camphor-10-sulfonic acid is in powdered form, they are highly recommended. All tested acids were recycled and their activity was studied under optimum conditions. This study revealed that all the acids tested can be recycled at least three times and, further, (1R)-(-)-camphor-10-

sulfonic acid and 1-propanesulfonic acid can be utilised six times. Using chromosulfuric acid to compare the efficiency between chemical reactor and sonoreactor, it can be concluded that the esterification reaction is 12 times faster in the former. However, the advantage in using the sonoreactor is that it can handle high FFA content up to 20% but the catalyst dosage, such as sulfuric acid, must be as high as 2%. Conversion of hygroscopic organic acids such as *p*-toluenesulfonic acid monohydrate (PTSA) into deep eutectic solvent (DES) provides opportunity in the improvement of the esterification reaction, whereby a DES is synthesized by simply mixing a hydrogen bond donor with a salt. Three DESs based on PTSA using ammonium and phosphonium salts were investigated, and it was found that the ammonium-based DES has a higher catalytic activity. The hygroscopicity and the recyclability of DESs were improved, hence indicating their superiority over the heterogeneous acids. Through well established analysis, the biodiesel produced utilizing the different types of catalyst met the EN 14214 and ASTM D6751 standards.

ABSTRAK

Kajian ini memperkenalkan tiga bahan mentah baru bagi pengeluaran biodiesel iaitu minyak sawit mentah berasid (ACPO), minyak sawit mentah gred rendah (LGCPO) dan campuran minyak sawit industri (MIPO).MIPO ialah campuran ACPO dan minyak sawit kumbahan (SPO). Bahan-bahan mentah ini boleh dikategorikan berdasarkan komposisi asid lemak bebas dan sifat fizikal. Bahan-bahan mentah tersebut mempunyai kandungan asid lemak tepu dan tidak tepu yang sama. Julat berat molekul untuk bahan-bahan mentah yang berasaskan minyak sawit ialah 816-836 (g/mol). Ciri-ciri bahan mentah tersebut menunjukkan bahawa ia tidak boleh dimakan dan diklasifikasikan sebagai minyak gred rendah. Proses pra-rawatan diperlukan untuk menukarkan asid lemak bebas (FFA) kepada asid lemak metil ester (FAME) sebelum diproses sebagai biodiesel. Penghasilan pemangkin boleh dianggap sebagai sumbangan besar dalam pra-rawatan pemprosesan biodiesel. Pelbagai jenis asid telah disaring dan asid homogenous yang berikut telah dipilih untuk pengomptimaan seterusnya: asid etanasulfonik, asid metanasulfonik, asid trifluorometanasulfonik, asid benzenasulfonik, asid (1R)-(-)-camphor-10-sulfonik, asid 1-propanasulfonik dan asid kromosulfurik. Keadaan optimum untuk semua pemangkin adalah lebih kurang sama dari segi pemuatan methanol, suhu tindak balas dan masa tindak balas kecuali dos pemangkin. Asid yang lebih kuat memerlukan dos antara 0.75% berat hingga 1% sementara asid organik yang lebih lemah memerlukan dua kali ganda dos untuk mengurangkan kandungan FFA ke tahap yang boleh diterima. Penggunaan asid yang mengandungi atom fluorin, seperti asid trifluorometanasulfonik tidak digalakkan dalam industri biodiesel kerana isu keselamatan dan tindak balas dengan udara. Dalam keadaan normal, asid benzenasulfonik wujud dalam keadaan pepejal dan asid (1R)-(-)-camphor-10-sulfonik dalam bentuk serbuk, kedua-duanya amat disyorkan. Semua asid yang diuji telah dikitar semula dan aktiviti asid tersebut dikaji di bawah keadaan optimum. Kajian ini

mendedahkan bahawa semua asid yang diuji boleh dikitar semula sekurang-kurangnya tiga kali. Tambahan pula, asid (1R)-(-)-camphor-10-sulfonik dan asid 1-propanasulfonik boleh digunakan sebanyak enam kali. Asid kromosulfurik yang digunakan untuk perbandingan effisiensi antara reactor kimia dan sonoreaktor, menunjukkan bahawa tindak balas esterifikasi dalam reactor kimia adalah 12 kali lebih cepat. Namun begitu, kelebihan dalam menggunakan sonoreaktor ialah kebolehan mengendalikan kandungan FFA yang tinggisehingga 20% tetapi dos pemangkin seperti asid sulfurik mestilah sebanyak 2%. Penukaran asid organic higroskopik seperti asid *p*-toluenasulfonik (PTSA) kepada pelarut *deep eutectic solvent* (DES) menambahbaik tindak balas esterifikasi, di mana DES disintesis dengan mencampurkan penderma ikatan hydrogen dengan sejenis garam. Tiga DES, berasaskan PTSA menggunakan garam ammonium dan fosfonium telah diselidik, dan didapati bahawa DES berasaskan ammonium mempunyai aktiviti pemangkinan yang lebih tinggi. Sifat higroskopi dan kebolehkitaran semula DES telah diperbaiki, seterusnya menunjukkan kelebihan DES ke atas asid heterogenous. Menerusi analisis yang mantap, biodiesel yang dihasilkan dengan menggunakan pelbagai jenis pemangkin telah menepati piawaian EN 14214 dan ASTM D6751.

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SYMBOLSAND ABBREVIATIONS

ACPO	Acidic crude palm oil
SPO	Sludge palm oil
LGCPO	Low-grade crude palm oil
CPO	Crude palm oil
MIPO	Mixed industrial palm oil
LGPO	Low-grade palm oil
FFA	Free fatty acid
FAME	Fatty acid methyl ester
ESA	Ethanesulfonic acid
MSA	Methanesulfonic acid
TFMSA	Trifluoromethanesulfonic acid
BZSA	Benzenesulfonic acid
10-CSA	(1R)-(–)-camphor-10-sulfonicacid
1-PSA	1-propanesulphonic acid
CSA	Chromosulfuric acid
PTSA	*p*-toluenesulfonic acid monohydrate
DES	Deep eutectic solvent
EN	European Committee for Standardization
ASTM	American Society for Testing and Materials
WCO	Waste cooking oil
LCC	Lignin-derived carbonaceous catalyst
KOH	Potassium hydroxide
NaOH	Sodium hydroxide
ILs	Ionic liquids

ChCl	Choline chloride
P-DES	Phosphonium-based deep eutectic solvent
DEAC-DES	N,N-diethylenethanol ammonium chloride-based deep eutectic solvent
ChCl-DES	Choline chloride based deep eutectic solvent

CHAPTER 1: INTRODUCTION

1.1 Overview

The scarcity and depletion of conventional fossil fuels resulted in a surge of interest in exploring new bioresource fuel alternatives. Biodiesel is receiving considerable attention as a renewable fuel alternative due to the continuous upsurge in fossil fuel prices, their limited resources, and environmental concerns. Recently, a mixture of soybean and rapeseed oils was used to produce biodiesel (Qiu et al., 2011). However, these two types of oils are edible oils, which makes them unsuitable for biodiesel production. Jatropha oil *(Jatrophacurcas)* (Kumartiwari et al., 2007; Wang et al., 2011; Lian et al., 2012; Atadashi et al., 2012; Prasad et al., 2012) and microalgae lipid (Huang et al., 2010) were proposed in many previous studies to produce biodiesel. The preparation of these two types of oils needs cultivation and multi-stage units for extraction and refining. These extra pretreatment operations will increase the cost of raw material as well as that of the production cost. Various studies proposed waste cooking oil (WCO) as an economical source to produce biodiesel fuel (Canakci and Van Gerpen, 2001; Kulkarni and Dalai, 2006; Canakci, 2007; Berrios et al., 2007). However, WCO is not available in bulk quantities in many countries and its collection is a difficult bottle-neck issue. Moreover, WCO can be regenerated and reused for industrial applications such as soap production due to their better purity compared to by-product oil from industrial vegetable oil mills such as palm oil fatty acid distillateand sludge palm oil (SPO)(Chongkhong et al., 2007; Hayyan 2010a; 2011). Therefore, looking for available, non-edible waste agro-industrial oils will be promising from a commercial point of view. Malaysia is the biggest palm oil producer and exporter in the world (Kalam and Masjuki, 2002). Therefore, palm oil and its by-products have potential use as a biodiesel starting

material. On a commercial scale, palm oil is used as a food product; therefore, conversion of refined palm oil to biodiesel will be very expensive. Thus, exploring new bio-sources for fuel production is one of the priorities of industrial-oriented research. Alternatively, there are large amounts of by-products and low-grade palm oil with high FFA content produced from palm oil mills. These could be converted to fatty acid methyl esters (FAME)or biodiesel. Raw material generated from industrial mills will increase the production rate of exported biodiesel in countries such as Malaysia and Indonesia. In addition, the use of agro-industrial low-grade oil can reduce the total cost of biodiesel production dramatically. Low cost industrial raw materials usually contained high acidity due to the high amounts of free fatty acid (FFA). Different technologies are available for biodiesel production, including dilution, micro-emulsification, pyrolysis (Balat and Balat, 2010; Singh and Singh 2010), and using supercritical methanol (Varma and Madras, 2006; Pinnarat and Savage, 2008; Alenezi et al., 2010). The high equipment cost, energy consumption and the low quality of product are the main obstacles upon the economic application of these technologies to produce biodiesel fuel (Lin et al., 2011). Chemical reactions such as esterification and transesterification are the typical methods for biodiesel production (Santori et al., 2012; Borges and Díaz, 2012). Therefore, a great deal of scientific literature deals with producing biodiesel using these common chemical reactions.

There are many types of reactors for biodiesel production such as chemical reactor, sonoreactor, and microwave reactor (Hayyan et al., 2011; Stavarache et al., 2005; Stavarache et al., 2006). The chemical reactor and sonoreactor are safer compared to the microwave reactor due to high energy used for operation of microwave reactor. Due to economical aspects, biodiesel production using chemical reactor is the most

commonly applied technology in biodiesel industry. To date, there is not much study reporting a comparison between chemical reactor and sonoreactor using the same conditions and raw material for biodiesel production. This comparison needs more consideration to highlight the merits of both technologies.

The key point in conducting efficient biodiesel production reactions is the catalytic activity of the used catalyst. Hence, catalyst development gains high attention by the scientific and industrial communities. The studies in this field target improving the economy and production quality and throughput that can be applied in an industrial scale. Besides, an economical catalyst with environmental merits will be more industrially recommended in order to fulfill the green applied energy goals. Biocatalysts such as lipase, was widely used for biodiesel preparation (Li and Yan, 2010; Chattopadhyay et al., 2011). The high cost of the enzyme is the main problem for its commercial utilization as a biocatalyst in chemical reactions. Different types of acidic solid catalysts were applied in the pre-treatment of acidic oils such as acid exchange resins (Tesser et al., 2010), ferric sulfate (Wanget al., 2007) and multi-wall carbon nano tubes-based solid acid catalysts (Shu et al., 2009; 2010). Recently, a lignin-derived carbonaceous catalyst (LCC) was used to reduce the FFA content in acidic soybean soapstock for biodiesel production (Guo et al., 2012). The reaction time for the esterification reaction using LCC was too long compared to the corresponding homogenous catalyst. In addition, LLC needs special equipment and conditions for the catalyst preparation. The common acidic catalysts used for the esterification reaction are *p*-toluenesulfonic acid (PTSA) and sulfuric acid (Di Serio et al., 2008; Hayyan et al., 2010a; 2011). These types of acids are readily commercially available and can be used directly in the synthesis of materials and chemical reactions.

The common industrial catalyst for the esterification reaction is sulfuric acid (Haas et al., 2003; Lin et al., 2009; Hayyan et al., 2011). Potassium hydroxide (KOH) or sodium hydroxide (NaOH) are the typical catalysts used for the transesterification reaction (Canakci, 2007; Atadashi et al., 2012). The main obstacle for using a homogeneous catalyst in the biodiesel production is the separation of catalyst and purification of product. Thus, recycling development is one of the main critical points for the application of homogeneous catalysts in the biodiesel industry.

Recently, ionic liquids (ILs) and their applications have triggered the interest of researchers in numerous fields (Olivier-Bourbigou et al., 2010; Hayyan et al., 2010b). They have been applied successfully in biological, chemical, and electrochemical applications (Yue et al., 2011; Hayyan et al., 2012; Xue et al., 2006), including for biodiesel production (Elsheikh et al., 2011). ILs have numerous advantages, such as their undetectable vapor pressure and liquidity at a wide temperature range (Xue et al., 2006; Naushad et al., 2012). ILs are usually expensive and unavailable at industrial scale.

Deep eutectic solvents (DESs) can be categorized as low cost solvents in comparison to ILs (Hayyan et al., 2013). DESs share many merits and physical properties with ILs (Kareem et al., 2010; Hayyan et al., 2012b). In addition, DES preparation is relatively straight forward in comparison to conventional ILs (Cooper et al., 2004). Choline chloride (ChCl) is the common salt used as the main ingredient in a wide range of available DESs. The ChCl-urea based DES was one of the first reported in literature, and was used later in numerous applications (Abbott et al., 2003; 2007; Wang et al., 2010). While DESs have been tested in downstream purification of biodiesel (Hayyan, 2010a), their application in the actual biodiesel production demands further investigation.

Consequently, catalyst development for new sources of raw materials for biodiesel production is important in the integration of economic technology in biodiesel industry. Therefore, this study will focus on the identification of new raw materials, investigation of new catalysts, comparison between chemical and sonoreactor and the application of DESs for biodiesel production.

1.2 Problem statement and significance of study

Producing biodiesel from low grade oils faces many practical obstacles such as their high content of free fatty acids (FFA), water content and other impurities. Due to the high FFA content, alkali catalyzed transesterification forms soap and the resulting emulsification causes separation problems and consequently wastage of the oils. The use of low cost feedstock such as low-grade oils for biodiesel production requires an additional pre-treatment step before the transesterification process.

Catalyst development is an important stage in biodiesel production. This study therefore introduced different types of homogenous catalysts for esterification reaction. Homogenous catalysts were used as catalysts in esterification reactions; however, their hygroscopic nature, storage and handling difficulties prevented their commercial applications. Therefore, it is very important to target a new and active catalyst which can be recycled many times. Conversion of solid organic acids such as PTSA into DES using simple technique will provide good opportunity to improve various types of acids used in numerous chemical reactions. In addition, catalysts based on DESs will be successful alternatives to heterogeneous catalysts and can reduce the downstream operations by elimination of filtration and catalyst pretreatment.

1.3 Research objectives

To summarise, the objectives of the present study are:

1- To identify and characterize new industrial raw materials from palm oil mills for biodiesel production.

2- To screen conventional and new acidic catalysts and select the most active catalyst for esterification reaction.

3- To develop a technique for recycling of homogenous acid catalysts.

4- To compare between chemical reactor and sonoreactor in terms of efficiency and FFA conversion to FAME.

5- To improve the homogeneous acid catalysts via conversion of PTSA to DES using different types of phosphonium and ammonium salts and to optimize the operating conditions for the esterification reaction.

1.4 Study Plan

The study covers 5 major topics:

Topics	**Published papers no.**
(i) Identification and characterization of available industrial raw materials**.**	**1, 2, 4, 5, 6 and 11**
(ii) Investigation of optimum conditions of selected homogenous catalysts for esterification.	**1, 2 3, 4, 5, 6 and 7**
(iii) - Recycling homogenous catalysts after esterification reaction. - Propose flowchart with recycling system to produce biodiesel.	**1, 2, 4, 5, 6, 10, 11 and 12**
(iv) - Comparison between sonoreactor and chemical reactor. - Studies on FFA reduction in high FFA raw material such as low-grade palm oil using sonoreactor.	**7, 8, and 9**
(v) Synthesis and study the catalytic activity of phosphonium and ammonium-based deep eutectic solvent in the treatment of low grade crude palm oil for biodiesel production.	**10, 11 and 12**

1.5 List of published papers and their content

1- Bioresource Technology (Impact Factor 5.039).

Adeeb Hayyan, Farouq S. Mjalli, Mohd Ali Hashim, Maan Hayyan, Inas M. AlNashef, Saeed M. Al-Zahrani, Mohammed A. Al-Saadi. Ethanesulfonic acid-based esterification of industrial acidic crude palm oil for biodiesel production. *Bioresource Technology* 102 (2011) 9564–9570. (ISI-Cited Publication/ Elsevier).

Abstract

An industrial grade acidic crude palm oil (ACPO) pre-treatment process was carried out using ethanesulfonic acid (ESA) as a catalyst in the esterification reaction. ESA was used in different dosages to reduce free fatty acid (FFA) to a minimum level for the second stage of biodiesel production via alkaline transesterification reaction. Different process operating conditions were optimized such as ESA dosage (0.25–3.5% wt/wt), methanol to ACPO molar ratio (1:1–20:1), reaction temperature (40–70^{o}C), and reaction time (3–150 min). This study revealed the potential use of abundant quantities of ACPO from oil palm mills for biodiesel production. The lab scale results showed the effectiveness of the pre-treatment process using ESA catalyst. Three consecutive catalyst recycling runs were achieved without significant degradation in its performance. Second and third reuse runs needed more reaction time to achieve the target level of FFA content. Esterification and transesterification using ESA and KOH respectively is proposed for biodiesel industrial scale production. The produced biodiesel meets the international standards specifications for biodiesel fuel (EN 14214 and ASTM D6751).

2- Chemical Papers (Impact Factor 1.193).

Adeeb Hayyan, Farouq S. Mjalli, Mohamed E.S. Mirghani, Mohd Ali Hashim, Maan Hayyan, Inas M. AlNashef, Saeed M. Al-Zahrani. Treatment of acidic palm oil for fatty acid methyl esters production. *Chemical Papers,* 66 (2012) 39–46. (ISI-Cited Publication/ Springer).

Abstract

Acidic crude palm oil (ACPO) produced from palm oil mills with an acid value of 18 mg g^{-1} was considered to be a possible feedstock for biodiesel production. Due to its high acidity, conventional transesterification cannot be applied directly for biodiesel production. Methane sulphonic acid (MSA, CH_3SO_3H) is used to reduce the acidity prior to the alkaline transesterification reaction. The laboratory-scale experiments involved an MSA to ACPO dosage of 0.25–3.5%, a molar ratio (methanol to ACPO) from 4:1 to20:1, reaction temperature of 40–80 ºC, reaction time of 3–150 min, and stirrer speed of 100–500 min^{-1}. The optimum esterification reaction conditions were 1% of catalyst to ACPO, with a molar ratio of methanol to ACPO of 8:1, a stirring speed of 300 min^{-1}, for 30 min and at 60ºC. Under these conditions, the FFA content was reduced from 18mg g^{-1} to less than 1 mg g^{-1} and with a yield of 96%. The biodiesel produced met the EN14214standard specifications. MSA was recycled for three times without losing its activity. The biodiesel produced in a two-stage process has a low acid value (0.14 mg g^{-1}).

3- The Korean Journal of Chemical Engineering (Impact Factor: 1.241).

Adeeb Hayyan, Mohamed E.S. Mirghani, Mohd Ali Hashim, Maan Hayyan, Inas M. AlNashef, Esterification of sludge palm oil using trifluoromethanesulfonic acid for preparation of biodiesel fuel. *The Korean Journal of Chemical Engineering*, 30 (2013) 1229-1234. (ISI-Cited Publication/Springer).

Abstract

Trifluoromethanesulfonic acid (TFMSA) was used to reduce the high free fatty acids (FFA) content in sludge palm oil (SPO). The FFA content of SPO was converted to fatty acid methyl ester (FAME) via esterification reaction. The treated sludge palm oil was used as a raw material for biodiesel production by transesterification process. Several working parameters were optimized, such as dosage of catalyst, molar ratio, reaction temperature and time. Less than 2% of the FFA content was the targeted value. The results showed that the FFA content of SPO was reduced from 16% to less than 2% using the optimum conditions. The yield of the final product after the alkaline transesterification was 84% with 0.07% FFA and the ester content was 96.7%. All other properties met the international standard specifications for biodiesel quality such as EN 14214 and ASTM D6751.

4- International Journal of Green Energy (Impact Factor: 1.469).

Adeeb Hayyan, Farouq S. Mjalli, Mohd Ali Hashim, Maan Hayyan, Inas M. AlNashef, Talal Al-Wahaibi, Yahya M. Al-Wahaibi. A solid organic acid catalyst for the pre-treatment of low grade crude palm oil and biodiesel production. *International Journal of Green Energy*, 11 (2014) 129-140. (ISI-Cited Publication/Taylor & Francis).

Abstract

Industrial low-grade crude palm oil (LGCPO) generated from industrial palm oil mills must be pretreated before utilizing it as a biodiesel raw material. The pretreatment of LGCPOwas conducted using benzenesulfonic acid (BZSA) as solid organic acid catalyst. Batch pretreatment of LGCPO was carried out to study the influence of BZSA dosage (0.25–3.5%wt/wt), methanol molar ratio to LGCPO (4:1–20:1), temperature (40–80 ^{o}C), and reaction time (3–150 min). The effects of those parameters on the free fatty acid content, and the yield of pretreated LGCPO were reported. This study illustrated the feasibility of using LGCPO from palm oil mills to produce biodiesel. The biodiesel produced from LGCPO meets the international standards (ASTM D6751 and EN 14214). Three times recycling of BZSA was achieved without appreciable degradation in its activity. This study introduces a possible batch esterification process using BZSA followed by an alkaline transesterification reaction for a possible future industrial application.

5- Chemical Engineering Science (Impact Factor 2.613).

Adeeb Hayyan, Mohd Ali Hashim, Maan Hayyan. Agro-industrial acidic oil as a renewable feedstock for biodiesel production using (1R)-(-)-camphor-10-sulfonic acid, *Chemical Engineering Science.* 116 (2014) 223-227.(ISI-Cited Publication/ Elsevier).

Abstract

A mixture of low grade industrial oils such as acidic crude palm oil (ACPO) and sludge palm oil (SPO) was used for biodiesel production. A novel organic acid, (1R)-(–)-camphor-10-sulfonic acid (10-CSA), was introduced as a catalyst for esterification reaction. 10-CSA shows high activity as a catalyst in the reduction of free fatty acid (FFA) and high conversion of fatty acid methyl ester (FAME). The effects of reaction temperature, reaction time and molar ratio on FFA reduction and FAME conversion were studied. The FFA content was reduced from 8% to less than 1% under optimum conditions. The final product (biodiesel fuel) produced from treated oils (ACPO and SPO) meets international biodiesel standards. This is the first time 10-CSA has been introduced as a catalyst for esterification reaction. This catalyst can treat a wide range of acidic raw materials for biodiesel production. 10-CSA is a promising catalyst and can be used for various chemical reactions.

6- BioEnergy Research (Impact Factor: 3.398).

Adeeb Hayyan, Mohd Ali Hashim, Maan Hayyan. Application of a novel catalyst in esterification of mixed industrial palm oil for biodiesel production. *BioEnergy Research* 8 (2015) 459-463 (ISI-Cited Publication/Springer).

Abstract

Mixed industrial palm oil (MIPO) is proposed in this study as a renewable and agro-industrial raw material to produce biodiesel fuel. MIPO was obtained by mixing of acidic crude palm oil with sludge palm oil. Due to the high level of free fatty acid (FFA) in MIPO (8.5%), esterification is needed to remove the acidity to the minimum level before biodiesel production. This is the first time 1-propanesulphonic acid (1-PSA) has been introduced as a catalyst for the pre-treatment of MIPO. Using optimum conditions, the FFA content was successfully reduced from 8.5% to less than 1%. The biodiesel produced meets the international standards (ASTM D6751 and EN 14214). 1-PSA is therefore a promising catalyst that can be used to treat various types of acidic oils.

7- **Bulgarian Chemical Communications (Impact Factor: 0.349).**

Adeeb Hayyan, Farouq S. Mjalli, Mohd Ali Hashim, Maan Hayyan, Inas M. AlNashef. Conversion of free fatty acids in low grade crude palm oil to methyl esters for biodiesel production using chromosulfuric acid. *Bulgarian Chemical Communications*. 45 (2013) 394 – 399. (ISI-Cited Publication).

Abstract

Chromosulfuric acid (CSA) was used as a new homogenous catalyst in the pre-treatment process to reduce the free fatty acids (FFA) content in LGCPO to the acceptable level for producing biodiesel via alkaline transesterification reaction. Chemical reactor was used for the esterification reaction. The results of esterification reaction showed that the FFA of LGCPO was reduced from 7.0 % to less than 1% under optimum operating conditions. The yield of the final product after the alkaline transesterification was 85% with 0.14 % FFA content and ester content 97.5% (mol mol^{-1}) which meets the international standard quality specifications for biodiesel.

8- Energy Sources, Part A: Recovery, Utilization, and Environmental Effects (Impact Factor: 0.358).

Adeeb Hayyan, Mohd Ali Hashim, Maan Hayyan, Inas M. AlNashef. Application of ultrasonic energy in the production of biodiesel from acidic crude palm oil using new homogenous catalyst. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, DOI:10.1080/15567036.2012.721057* (ISI-Cited Publication/Taylor & Francis).

Abstract

Acidic crude palm oil (ACPO) was used as a raw material for biodiesel production. Different types of acids were utilized in order to investigate the catalytic activity of weak and strong acids including chromosulfuric acid (CSA), sulfamic acid and formic acid. Ultrasonic energy (40 kHz) was used in the esterification reaction to reduce the high free fatty acid (FFA) in ACPO. CSA reduced FFA from 8.7% to less than 2%. CSA showed the highest catalytic activity in the reduction of FFA in ACPO compared with other homogeneous acids. The produced biodiesel meets the international biodiesel standards EN14214 and ASTM D6751.

9- Journal of Industrial and Engineering Chemistry (Impact Factor: 2.063).

Adeeb Hayyan, Mohd Ali Hashim, Mohamed E.S. Mirghani, Maan Hayyan, Inas M. AlNashef. Treatment of industrial low grade palm oil via esterification reaction using sonoreactor. *Industrial and Engineering Chemistry* 20 (2014) 2066–2070 (ISI-Cited Publication/ Elsevier).

Abstract

In this study, the reduction of free fatty acid (FFA) in low grade palm oil (LGPO) was conducted using sonoreactor at various sonication times, ranging from 30 to 300 min. Screening of various acids was reported and selected acid was considered for further study. The results found that strong acids such as sulfuric acid to be superior to other acids. The FFA content of LGPO decreased from 20% to less than 3%, using sulfuric acid at optimum conditions. Treated LGPO can be used as a new type of fuel for various applications such as biodiesel production.

10- Chemical Engineering Science (Impact Factor 2.613).

Adeeb Hayyan, Mohd Ali Hashim, Farouq S. Mjalli, Maan Hayyan, Inas M. AlNashef. A novel phosphonium-based deep eutectic catalyst for biodiesel production from low grade crude palm oil. *Chemical Engineering Science* 92 (2013) 81-88 (ISI-Cited Publication/ Elsevier).

Abstract

This study explores the possibility of producing low grade crude palm oil (LGCPO)-based biodiesel using a two-stage process in which a phosphonium-based deep eutectic solvent (P-DES) and an alkali are used as catalysts. The pre-treatment of LGCPO was conducted using a P-DES composed of a hydrogen bond donor (i.e. *p*-toluenesulfonic acid monohydrate) and a salt (i.e. allyltriphenylphosphonium bromide) as a novel recyclable catalyst. The P-DES was used in different dosages in thepresence of methanol to reduce the level of free fatty acids (FFA) to the acceptable limit for alkaline transesterification reaction. Batch pre-treatment of LGCPO was carried out to study the influence of P-DES dosage (from 0.25 to 3.5% wt/wt). The effects of other operating parameters such as molar ratio, reaction temperature and reaction time on FFA content reduction, yield of treated LGCPO and FFA to FAME conversion were studied. The P-DES showed high catalytic activity in the pre-treatment of LGCPO. The lab scale investigation proved the viability of esterification and transesterification of oil using P-DES and alkaline catalysts. The biodiesel produced from LGCPO meets the international standards (ASTM D6751 and EN 14214). Three to four times recycling runs of P-DES were achieved without losing its activity. This study introduces a new generation of catalysts for possible batch esterification reaction using P-DES followed by an alkaline transesterification reaction. Industrial flow chart was proposed in this study for biodiesel production and recycling of DES.

11- Industrial Crops and Products (Impact Factor: 3.208).

Adeeb Hayyan, Mohd Ali Hashim, Maan Hayyan, Farouq S. Mjalli, Inas M. AlNashef. A novel ammonium based eutectic solvent for the treatment of free fatty acid and synthesis of biodiesel fuel. *Industrial Crops and Products*, 46 (2013) 392-398. (ISI-Cited Publication/ Elsevier).

Abstract

In this work, low grade crude palm oil (LGCPO) with high free fatty acids (FFA) content is introduced as a possible biodiesel production feedstock alternative. The pre-treatment of LGCPO was conducted using ammonium-based deep eutectic solvent which consisted of hydrogen bond donor (i.e. *p*-toluenesulfonic acid monohydrate) (PTSA) and salt (i.e. N,N-diethylenethanol ammonium chloride) as a novel recyclable catalyst (DEAC-DES). The DEAC-DES was used in different dosages to reduce the level of FFA to the acceptable limit for biodiesel production. The esterification reaction was carried out to evaluate the effect of varying reaction operating conditions on the reduction of FFA content. The FFA content of LGCPO was reduced from 9.5% to less than 1% using optimum conditions. Four recycling runs of the DEAC-DES were achieved. The conversion of PTSA to deep eutectic solvent improved the recyclability of the acid and the physical properties such as the elimination of acid hygroscopicity. The LGCPO biodiesel fulfilled the international standards. This study demonstrates a potential route for biodiesel production from abundance LGCPO using DEAC-DES and an alkaline catalyst.

12- Journal of Cleaner Production (Impact Factor 3.590).

Adeeb Hayyan, Mohd Ali Hashim, Maan Hayyan, Farouq S. Mjalli, Inas M. AlNashef. A new processing route for cleaner production of biodiesel fuel using a choline chloride based deep eutectic solvent, *Journal of Cleaner Production* 65 (2014) 246-251. (ISI-Cited Publication/ Elsevier).

Abstract

In this study, the free fatty acids (FFA) content in acidic crude palm oil (ACPO) was converted to fatty acid methyl esters (FAME) using a choline chloride based deep eutectic solvent (ChCl-DES) for the first time. This DES is composed of a mixture of a hydrogen bond donor (i.e. *p*-toluenesulfonic acid monohydrate) and a salt (i.e. choline chloride). The pre-treatment esterification stage involved the use of ChCl-DES. A dosage of 0.75 mass ratio of ChCl-DES to ACPO resulted in reducing the FFA of ACPO from 9.00% to less than 1%. The molar ratio of methanol to oil was 10:1 (methanol to oil), at a temperature of 60 ^{o}C and within 30 min reaction time. Three recycling runs of ChCl-DES were achieved without significant loss in its activity. The yield of the final product after the alkaline transesterification was 92 wt% with 0.07% FFA and FAME content 96 mol%. All other properties have met the international standard specifications for biodiesel quality. The ChCl-DES can be used as a pre-treatment catalyst for a wide range of waste and acidic oils.

CHAPTER 2: LITERATURE REVIEW

This chapter was converted to a review paper and submitted to BioResources (ISSN: 1930-2126), which is ISI **Q1** Journal with impact factor **1.549**. Due to the importance and impact of this review paper to the readers of biodiesel fields, the journal editorial board has converted this paper as an invited review paper for publication in BioResources. The review paper was cemented and focused to present the related literature and the importance of the pre-treatment process of acidic raw materials used for biodiesel production. This review paper focuses on the main factors affecting the performance of pre-treating acidic raw materials for biodiesel production.

Developing a pre-treatment technique to process oils before conducting the transesterification reaction is essential to insure producing biodiesel within the international standard specifications. Selection of suitable raw material, economical pre-treatment process and proper reaction catalyst with high activity should be done carefully before applying the production technology. New developments in pre-treatment technologies and new generation of highly active and recyclable catalysts are still essential for improving product quality and reducing production cost. Other literature related to the objectives of this thesis was summarized in the introduction of each published paper.

CHAPTER 3: PUBLISHED PAPERS

3.1 List of published papers

[1] Bioresource Technology

Adeeb Hayyan, Farouq S. Mjalli, Mohd Ali Hashim, Maan Hayyan, Inas M. AlNashef, Saeed M. Al-Zahrani, Mohammed A. Al-Saadi. Ethanesulfonic acid-based esterification of industrial acidic crude palm oil for biodiesel production. *Bioresource Technology 102* (2011) 9564–9570.

[2] Chemical Papers

Adeeb Hayyan, Farouq S. Mjalli, Mohamed E.S. Mirghani, Mohd Ali Hashim, Maan Hayyan, Inas M. AlNashef, Saeed M. Al-Zahrani. Treatment of acidic palm oil for fatty acid methyl esters production, *Chemical Papers, 66* (2012) 39–46.

[3] The Korean Journal of Chemical Engineering

Adeeb Hayyan, Mohamed E.S. Mirghani, Mohd Ali Hashim, Maan Hayyan, Inas M. AlNashef, Esterification of sludge palm oil using trifluoromethanesulfonic acid for preparation of biodiesel fuel. *The Korean Journal of Chemical Engineering, 30* (2013) 1229-1234.

[4] International Journal of Green Energy

Adeeb Hayyan, Farouq S. Mjalli, Mohd Ali Hashim, Maan Hayyan, Inas M. AlNashef, Talal Al-Wahaibi, Yahya M. Al-Wahaibi. A solid organic acid catalyst for the pre-treatment of low grade crude palm oil and biodiesel production. *International Journal of Green Energy, 11* (2014) 129-140.

[5] Chemical Engineering Science

Adeeb Hayyan, Mohd Ali Hashim, Maan Hayyan. Agro-industrial acidic oil as a renewable feedstock for biodiesel production using (1R)-(-)-camphor-10-sulfonic acid, *Chemical Engineering Science. 116* (2014) 223-227.

[6] BioEnergy Research

Adeeb Hayyan, Mohd Ali Hashim, Maan Hayyan. Application of a novel catalyst in esterification of mixed industrial palm oil for biodiesel production, *BioEnergy Research, 8* (2015) 459-463.

[7] Bulgarian Chemical Communications

Adeeb Hayyan, Farouq S. Mjalli, Mohd Ali Hashim, Maan Hayyan, Inas M. AlNashef. Conversion of free fatty acids in low grade crude palm oil to methyl esters for biodiesel production using chromosulfuric acid. *Bulgarian Chemical Communications. 45*, (2013) 394 – 399.

[8] Energy Sources, Part A: Recovery, Utilization, and Environmental Effects

Adeeb Hayyan, Mohd Ali Hashim, Maan Hayyan, Inas M. AlNashef. Application of ultrasonic energy in the production of biodiesel from acidic crude palm oil using new homogenous catalyst. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, DOI:10.1080/15567036.2012.721057*

[9] Journal of Industrial and Engineering Chemistry

Adeeb Hayyan, Mohd Ali Hashim, Mohamed E.S. Mirghani, Maan Hayyan, Inas M. AlNashef. Treatment of industrial low grade palm oil via esterification reaction using sono-reactor. *Industrial and Engineering Chemistry.20* (2014) 2066–2070.

[10] Chemical Engineering Science

Adeeb Hayyan, Mohd Ali Hashim, Farouq S. Mjalli, Maan Hayyan, Inas M. AlNashef.
A novel phosphonium-based deep eutectic catalyst for biodiesel production from low grade crude palm oil. *Chemical Engineering Science, 92* (2013) 81-88.

[11] Industrial Crops and Products

Adeeb Hayyan, Mohd Ali Hashim, Maan Hayyan, Farouq S. Mjalli, Inas M. AlNashef.
A novel ammonium based eutectic solvent for the treatment of free fatty acid and synthesis of biodiesel fuel. *Industrial Crops and Products, 46,* (2013) 392-398.

[12] Journal of Cleaner Production

Adeeb Hayyan, Mohd Ali Hashim, Maan Hayyan, Farouq S. Mjalli, Inas M. AlNashef.
A new processing route for cleaner production of biodiesel fuel using a choline chloride based deep eutectic solvent, *Journal of Cleaner Production. 65* (2014)246-251.

CHAPTER 4: MAJOR FINDINGSAND CONCLUSIONS

4.1 Identification of new raw materials for biodiesel production

This study introduced new raw materials for biodiesel production, namely:

1) **Acidic crude palm oil (ACPO).**

   ACPO was described in the published papers 1, 2, 8, and 12.

2) **Low grade crude palm oil (LGCPO).**

   LGCPO was described in the published papers 4, 7, 9, 10, and 11.

3) **Mixture of low-grade oils such as ACPO mixed with sludge palm oil (SPO)**.

   These materials were described in the published papers 3, 5 and 6.

- Characterization of the abovementioned raw materials showed that these feedstocks are non-edible and industrial low-grade oils were comparable to crude palm oil (CPO) as shown in Table 4.1. Free fatty acid (FFA), moisture content and peroxide value are higher in comparison to CPO. The main obstacle against producing biodiesel from these raw materials is the high FFA content. It is found that a pre-treatment stage to convert the FFA into fatty acid methyl ester (FAME) is required before proceeding to other palm oil refinery processes or for biodiesel production.

Table 4.1: Characterization of ACPO, LGCPO, MIPO, SPO and CPO

Parameters	ACPO	LGCPO	MIPO	SPO[1]	CPO[2]
FFA (%)	8.6	7.0	8.5	22.33	3.20
Peroxide value (ml mol/kg)	7.45	7.5	7.73	1.52	0.70
Moisture content (%)	1.105	1.03	1.54	1.20	0.18
Iodine value, IV	56	55	56.7	53.4	52.00
Impurities (%)	0.056	0.05	0.058	0.05	0.03
Saponification value	197.0	198.0	192.4	190	195.7*
Unsaponification matter (%)	6.70	6.8	6.50	1.47	0.51*
Ash (%)	0.011	0.01	0.017	0.015	-
Acid value (mg KOH/mg)	17.20	14.23	18	48.88	4.70
DOBI (Index)	1.80	1.81	1.64	0.55	2.70
Molecular weight (g/mol)	827	816.9	836.65	823.9	821.9

[1](Hayyan et al., 2010a), [2](Tan et al., 2009), *(Let, 1993).

- The main fatty acids for all raw materials-based palm oil are oleic, palmitic, linoleic, and stearic acid. These types of fatty acids are the main constituents of palm oil (Sambanthamurthi et al., 2000). The fatty acid profiles of all raw materials are similar to CPO and they have almost balance between the content of saturated and unsaturated fatty acids. However, the total saturated fatty acids is slightly higher. It was reported that CPO with FFA content of 3.49% has 53.54% saturated fatty while the corresponding reported values of SPO were 22.33% FFA content with 47.17 wt% (Elsheikh et al., 2011; Hayyan et al., 2010a).

- The calculated molecular weight of ACPO, LGCPO, and MIPO is close to SPO and CPO. The molecular weight was based on the saponification value. The molecular weight rage of raw materials based palm oil is 816-836 (g/mol).
- Naturally, the ACPO, LGCPO, and MIPO exist as a viscous red liquid or semisolid form at room temperature (27 ± 2 ^{O}C) due to the high FFA and saturated fatty acids content compared to CPO or refined palm oil. Therefore, they have higher pour and cloud points as compared to low FFA content CPO. Consequently, these raw materials should be pre-heated before proceeding to the pre-treatment stage using the esterification reaction.
- ACPO, LGCPO, and MIPO have an FFA content higher from 7% up to 10%. Above this limit, the oil is considered as SPO. LGCPO has high FFA content, similar to ACPO. However, it has much lower quality due to the presence of unfavored impurities and the high moisture content. The main similarity between ACPO and LGCPO is the high FFA content. Due to this property, palm oil mills usually reject this raw material or alternatively conduct some pretreatment processing, chemical or physical pretreatment, before sending it to palm oil refineries. While MIPO is a mixture of ACPO and SPO. In the mixture of ACPO and SPO used in the present work, the percentage of SPO was very low in comparison to ACPO. A small portion of SPO, such as 8–10 wt% (SPO to ACPO), was sufficient to increase the ACPO from 4.8% to 8–9% due to high FFA content to SPO (e.g., 66%).
- These raw materials were considered as viable and available bioresources feedstocks generated from palm oil mills. Biodiesel to be produced from available industrial feedstock will decrease the production cost of biodiesel fuel, consequently increasing the value of low-grade palm oil and opening new markets

and new income sources for palm oil countries such as Malaysia and Indonesia. Production of biodiesel from low-grade palm oil using simple, cheap, safe, green, and environmental techniques will improve the role of biodiesel as an alternative fossil fuel.

4.2 Optimum conditions for homogenous acids using chemical reactor

- Many types of acids and chemicals were screened and reported in this study (Appendix A). It was found that there is no significant catalytic activity for majority of these acids. Acids with simple structure were more active in comparison to acids with long carbon chain and acids attached with salts.
- Sulfonic acids-based catalysts for esterification reaction were used in this study. Table 4.2 shows the summary of optimum conditions for all catalysts.

Table 4.2: Optimum conditions for different acid catalysts

No.	Acids name	Name of raw material	Initial FFA	Final FFA	Optimum conditions
1.	Ethanesulfonic acid	Industrial acidic crude palm oil	8.6%	<1%	0.75%, 10:1, 60 ^{o}C, 30 min
2.	Methanesulfonic acid	Acidic crude palm oil	9.0%	<1%	1%, 8:1, 60 ^{o}C, 30 min
3.	Trifluoromethanesulfonic acid	Sludge palm oil	16.0%	<2%	0.75%, 10:1, 60 ^{o}C, 40 min
4.	Benzenesulfonic acid	Low grade crude palm oil	9.3%	<1%	0.75%, 8:1, 60 ^{o}C, 30 min
5.	(1R)-(-)-camphor-10-sulfonic acid	Agro-industrial acidic palm oil	8.0%	<1%	1.5%, 10:1, 60 ^{o}C, 30 min
6.	1-propanesulphonic acid	Mixed industrial palm oil	8.5%	<1%	0.75%, 8:1, 60 ^{o}C, 30 min
7.	Chromosulfuric acid	Low grade crude palm oil	7.0%	<1%	0.75%, 10:1, 60 ^{o}C, 30 min

- The optimum conditions of all optimized catalysts using a chemical reactor were almost the same in terms of methanol loading, reaction temperature, and reaction time. The difference was mainly in the dosage of the catalyst. The treatment of raw materials with high FFA content such as SPO required more reaction time. The strong acids required0.75% or 1% to reduce the FFA content to less than 1%. On the other hand, the weak organic acids such as (1R)-(-)-camphor-10-sulfonic acid required a double dosage of strong organic acids to reach the acceptable FFA limit.
- Strong acids with shorter carbon chains attached with a sulfonic group showed more catalytic activity using lower dosage and at first 10 minutes of esterification reaction.
- Catalyst consumption can be defined as the mass of catalyst consumed per mass of synthesized product (Hayyan et al., 2010a), and the values for acids in this study were 7.80 mg/gm for 0.75% or 10.34 mg/gm for 1% or 19.16 mg/gm for 1.5%. The results showed that the esterification reaction using strong acids such as trifluoromethanesulfonic acid is a second-order reaction.
- Acids with fluorine atoms, such as trifluoromethanesulfonic acid, are not recommended in the biodiesel industry due to safety issues as well as unwanted reactions with air. In addition, these acids are costly. Therefore, simple-structure acids, such as methanesulfonic acid or ethanesulfonic acid, are preferred for the esterification of high FFA content.
- Although trifluoromethanesulfonic acid is considered a super acid, methanesulfonic acid without fluorine shows higher catalytic activity in

esterification reaction. This may be due to reaction of fluorine atoms with air. Reaction of fluorine with air results in contamination of water in the acid.

- Overall, strong mineral acids such as sulfuric acid appeared to be more active compared to strong organic acids. However, organic acid is relatively safer to be used in biodiesel industry.
- All reported acids in this study are promising catalysts that can be used to treat various types of acidic oils and can be applied in other types of chemical reactions. Nevertheless, since benzenesulfonic acid exists in solid form while (1R)-(-)-camphor-10-sulfonic acid exists in powder form, this study recommends these two acids to be used in pilot scale.

4.3 Comparison between chemical reactor and sonoreactor

- A sonoreactor can be used to treat the high FFA content. However, catalyst selection and long reaction time play important roles in the esterification of high FFA content using a sonoreactor.
- The optimum conditions of using chromosulfuric acid (CSA) in chemical reactor are 0.75%, 10:1, 60 ^{o}C at 30 min, while the optimum conditions for CSA in sonoreactor are 1%, 10:1 (methanol to oil), 60 °C at 360 min sonication time. Using CSA to compare the efficiency between chemical reactor and sonoreactor, it can be concluded that the esterification reaction is 12 times faster in the former.
- In the industrial scale, the chemical reactor is more economical in the production of biodiesel for low-grade oils. Nevertheless, there are also some

advantages upon application of the sonoreactor for biodiesel production such as esterification of a small quantity of acidic oils.

- This study discussed the impact of sonoreactor for the treatment of high FFA content (up to 20%). The main conclusion is that the sonoreactor can be used to treat the high FFA content; the most important point in the reduction of high FFA content using the sonoreactor is the selection of a catalyst with high catalytic activity.
- Raw materials with high FFA content needs a higher dosage of catalyst (2%) compared to the catalyst dosage required to treat the low FFA content such as 8-10%, which needs only 1% of a strong acid.
- This study showed that the sonoreactor can be used to treat the high FFA content. However, catalyst selection plays very important role in esterification of high FFA content using a sonoreactor.
- This study reported the mechanism of esterification using sonoreactor. Ultrasonic energy was used to enhance theacid catalyst (sulfuric acid) to protonate the carbonyl group toward nucleophilic attack via waves generated from ultrasonic cleaner. When ultrasound operated for a certain frequency, the waves will start to vibrate the FFA of LGPO with reactants include methanol and the catalyst. This vibration will provide such mixing or contacting between FFA and the reactants. The vibration with temperature will enhance the esterification reaction and speed it up. Hence, ultrasonic cleaner can be considered as reactor (sonoreactor).
- During esterification reaction micro-emulation will be formed between FFA with reactants due to the random distribution of ultrasound waves and cavitation bubbles generated in the sonoreactor. There are many factors

effecting the esterification reaction in sonoreactor such as temperature, time of sonication and the frequency rate.

4.4 Deep eutectic solvents for esterification reaction

- Many types of sulfonic acids, such as *p*-toluenesulfonic acid monohydrate (PTSA), have a hygroscopic nature. The hygroscopicity is a disadvantage for the application of acids in chemical reactions and biodiesel production. This is because downstream processing required removal of traces of water from the acids. It is well known that many types of acids and ionic liquids (ILs) will lose their activity and their special phyco-chemical properties when they are used in open areas due to high reactivity or hygroscopicity with water in the air. Hence, a simple method to improve the physical properties of acids is much needed. This study converted strong organic acid such as PTSA into a deep eutectic solvent (DES). DESs are categorized as a low cost solvents and an alternative to ionic liquids (ILs). DESs can be in liquid or jelly form and they have a much lower melting point than the corresponding values of the individual constituting compounds (salt and hydrogen bond donors).

- DESs share many merits and physical properties with ILs. In addition, DES preparation is very simple compared to conventional ILs. DESs based on a mixture of PTSA and phosphonium or ammonium salt is an alternative to ILs. Hayyan et al., (2013a; 2013b) found that there was no toxic effect on the selected bacteria for ammonium-based DESs. On the other hand, the prepared DESs from phosphonium salt had a higher toxicity compared to ammonium-based DESs (Hayyan et al., 2013b). Hence, this study focused more in ammonium-based DES.

- Generally, DES is not considered as a type of IL. This is supported by Zhang et al. (2012), as they mentioned that "DES cannot be considered as ILs because: DESs are not entirely composed of ionic species and because DES can be obtained from non-ionic species".
- DES made from allyltriphenylphosphonium bromide mixed with PTSA at a ratio of 1:3 was in a jelly/viscous form at room temperature and had a yellow colour. The melting point of this DES was in the range of 43–47 ^{O}C. Introducing new salt can be considered one of the essential novelties. Consequently, many related studies are yet to be conducted in this field. Allyltriphenylphosphonium bromide-based DES will be applied in other applications and will extend the range of common salts.
- DES made from N.N-diethylenethanol ammonium chloride mixed with PTSA at a ratio of 1:3 had a white-turbid colour and a jelly-viscous form at room temperature. The melting point was measured and it was in the range of 38–45 ^{O}C.
- DES made from choline chloride mixed with PTSA at a ratio of 1:3 had a white-light grey colour and a viscous jelly form at room temperature. The melting point was measured and it was in the range of 37–44 ^{O}C.
- DESs have almost similar optimum conditions as shown in Table 4.3, and this gives an indication that the role of the salt is inert (Appendix A), and the main contributor in the reaction is the hydrogen bond donor, such as PTSA. However, a higher dosage of DESs is highly recommended for the esterification reaction to reduce the FFA to the acceptable limit.

Table 4.3: Optimum conditions of different DESs for the treatment of free fatty acid

No.	Acids name	Raw material used	Initial FFA	Final FFA	Optimum dosage
1.	Phosphonium-based deep eutectic catalyst	Low grade crude palm oil	9.3%	<2%	1%, 10:1, 60^{o}C, 30 min
2.	N,N-diethylenethanol ammonium chloride-based deep eutectic solvent	Low grade crude palm oil	9.5%	<1%	0.75%, 8:1, 60^{o}C, 30 min
3.	Choline chloride based deep eutectic solvent	Acidic crude palm oil	9.0%	<1%	0.75%, 10:1, 60^{o}C, 30 min

- Ammonium-based DESs have a higher catalytic activity compared to phosphonium-based DESs (Table 4.3). N.N-diethylenethanol ammonium chloride-based DES is the most active compared to choline chloride-based DESs.
- The optimum conditions using N.N-diethylenethanol ammonium chloride-based DES are similar to results using 1-PSA and BZSA for the reduction of FFA content.
- The recyclability of phosphonium-based DES is slightly higher than ammonium-based DES. The improvement of recyclability of DESs was due to the hydrogen bonding between PTSA and salts. The sulfonic group (SO_3H) is the intrinsic substance responsible for the esterification reaction. Due to hydrogen bonding with this group, the molecules will be more stable towards moisture. The molecules of DESs will also be bigger compared to PTSA molecules, and this can be another reason for recyclability improvements.
- The most stable DES after a long period of storage was the DES made from allyltriphenylphosphonium bromide, followed by DES made from N.N-diethylenethanol ammonium chloride. Choline chloride was not a stable DES after long storage at room temperature. Because DESs can be synthesized in such a

way that they are in solid form at room temperature, the storage and transport is much easier than in powdered or liquid forms.

4.5 Recyclability of different types of homogenous acids and DESs.

- The viability of using the catalyst in an economical way is determined by the frequency of its recycling. Successful recycling technology can lead to a significant reduction in the total cost of the pretreatment process. Recyclability of strong acids in liquid form is not mentioned in the literature. This study shows that there is the possibility of recycling the homogenous acids at least three times. The polarity differences between low-grade palm oil compared to methanol and acids can explain the philosophy of recyclability of liquids acids. The acids in liquid form can be recycled more than three times, based on the type of acid and its catalytic activity. 10-CSA and 1-PSA can be utilised six times.
- The loss of catalysts during recycling may be one of the primary reasons for the activity reduction of the catalyst. However, the viability of acid recycling depends solely on the catalyst separation efficiency.
- Acid and methanol are less dense than low-grade palm oil, and due to this, the acid mixed with methanol floats on top of the oil. These two phases make the separation process easy and efficient because simple gravity separation using a funnel is sufficient to separate the two layers. Separation via centrifugation is highly recommended as it requires a shorter period.

- Water generated as a by-product of the esterification reaction. This water is mixed with methanol and acid at the end of the esterification reaction. However, the amount of water generated from the reaction is very low, and it can be considered as negligible.

- Development of a simple procedure for recycling homogenous acids will add a very important advantage for homogenous acids to be used in the treatment of high FFA content of a wide range of acidic oils. This technology will also increase the application of homogenous acids in other chemical reactions.

4.6 Production of biodiesel from low-grade palm oil

- The main fatty acid compositions of biodiesel from ACPO, LGCPO and MIPO were C18:1, C16:0, C18:2 and C18:0. Palmitic acid and oleic acid had the highest fatty acid concentration in the FAME of ACPO, LGCPO and MIPO.
- The two types of fatty acids (palmitic acid and oleic acid) were in the highest concentration in the two types of oils. Saturated fatty acids such as palmitic acid are unfavourable for use in cold countries due to the crystallization phenomena of fuel during storage in cold conditions. In addition, saturated fatty acids are results of higher cloud and pour-points of fuels.
- Palmitic acid and other saturated fatty acids possess useful properties for hot countries and can increase the cetane number and reduce oxidation. Thus, the produced biodiesel from ACPO, LGCPO and MIPO is recommended in hot countries.

- The phosphorus value represent the phosphatide (gum) content in the fuel, and it was found at a very low concentration. The flashpoint and copper strip corrosion tests were found to be highly suitable as operational safety properties for biodiesel compared with petroleum diesel.
- The cetane number was high compared to petroleum diesel, which gave a significant advantage to the use of ACPO biodiesel as a blend with petroleum diesel. Other properties of purified biodiesel from ACPO met to the European and American standards (EN 14214 and ASTM D6751) for biodiesel fuel. The produced biodiesel was very clean, with high quality characteristics. This reflects the efficiency of the pre-treatment process using the different types of acids and DESs.
- The copper strip corrosion test and the sulfated ash test indicated that no traces of acid catalysts were present in the produced biodiesel. The high purity of biodiesel fuel showed the effectiveness of the proposed process using esterification and transesterification reactions.
- The findings achieved in this work show that the biodiesel produced from ACPO, LGCPO and MIPO met the European standard specifications, but the ester content of the treated oils was slightly lower than the international standard limit. This can be further studied by optimizing the transesterification reaction.

CHAPTER 5: RECOMMENDATIONS

- More attention should be given to investigate new types of catalysts for the esterification reaction. Further research is necessary to examine these types of catalysts and DESs for acidic reactions.
- Study of the structure and mechanisms of DES formation are needed to understand the physical properties and the catalytic activity of such DESs. The molecular chemistry interaction between salt and hydrogen bond donors is a missing gap in the field of DESs and their applications.
- Kinetics study for esterification reaction using the reported acids and DESs is recommended. All reported acids and DESs in this study can be used for the treatment of wide range of acidic oils and as catalysts for transesterification reaction of refined or treated oils or fats for direct biodiesel production.
- To investigate the advantages and disadvantages of DESs for biodiesel production, the physical properties, toxicity and biodegradability of DESs are required.
- Further research is needed to improve the physical properties of trifluoromethanesulfonic acid.
- Further studies are required to investigate the use of ultrasonic energy to treat acidic oils using various acidic catalysts to produce products such as biodiesel and glycerol. Studies on the kinetics of the esterification reaction using sonoreactors are also necessary.

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Appendix A: List of chemicals used for screening study

Screening of different types of acids and salts used for esterification reaction (initial FFA content is 8.5%-9.5%) using 10% wt of acid to oil, 10:1 molar ratio, 60ºC at 3 hours reaction time.

No.	Chemical name	Final FFA	Catalytic activity
1.	Methanol only without catalyst	6.5%	Not Active
2.	Sulfuric acid	0.2%	Active
3.	*P*-toluensulfonic acid monohydrate	0.3%	Active
4.	Ethanesulfonic acid	0.3%	Active
5.	Methanesulfonic acid	0.3%	Active
6.	Trifluoromethanesulfonic acid	0.3%	Active
7.	Benzenesulfonic acid	0.3%	Active
8.	(1R)-(-)-camphor-10-sulfonic acid	0.65%	Active
9.	1-propanesulphonic acid	0.34%	Active
10.	Chromosulfuric acid	0.33%	Active
11.	Isoquinoline-5-sulfonic acid	6.38%	Not Active
12.	Piperazine-1,4-bis (propane sulfonic acid) buffer substance	7.24%	Not Active
13.	Decane-1-sulfonic acid sodium salt	7.1%	Not Active
14.	(1R)-(-)-10-camphorsulfonic acid ammonium salt	9.25%	Not Active
15.	1,2-Naphthoquinone-4-sulfonic acid sodium salt	8.11%	Not Active
16.	Poly (2-acrylamido-2-methyl-1-propane sulfonic acid) solution	5.91%	Not Active
17.	3-chloro-2-hydroxy-1-propanesulfonic acidsodium salt hydrate	7.23%	Not Active
18.	Sulfanilic acid	6.29%	Not Active
19.	Amidosulfuric acid	5.87%	Not Active
20.	Sulphamic acid	6.8%	Not Active
21.	3-Amino-1-propanesulfonic acid	8.27%	Not Active

22.	3-Aminobenzenesulfonic acid	7.08%	Not Active
23.	1-Aminobenzene-3-sulfonic acid	7.15%	Not Active
24.	4-Aminonaphthalene-1-sulfonic acid	6.68%	Not Active
25.	3-Amino-4-methoxybenzenesulfonic acid	8.98%	Not Active
26.	2-(Cyclohexylamino)ethanesulfonic acid	8.35%	Not Active
27.	7-Amino-4-hydroxy-2-naphthalenesulfonic acid	6.59%	Not Active
28.	3-(Cyclohexylamino)-1-propanesulfonic acid (CAPS)	8.67%	Not Active
29.	N-[Tris(hydroxymethyl)methyl]-3-aminopropanesulfonic acid (TAPS)	7.20%	Not Active
30	4-Morpholinepropanesulfonic acid (MOPS)	7.54%	Not Active
31.	2-(Cyclohexylamino)ethanesulfonic acid(CHES ULTROL Grade)	7.11%	Not Active
32.	Aminomethanesulfonic acid	6.36%	Not Active
33.	1-amino-2-hydroxy-4-naphthalene sulfonic acid	6.15%	Not Active
34.	4-Aminonaphthalene-1-sulfonic acid sodium salt	7.43%	Not Active
35.	5-Amino-2(p-amino anilino) benzene sulfonic acid	7.20%	Not Active
36.	3-(Trimethylsilyl)-1-propanesulfonic acid sodium salt	5.98%	Not Active
37.	8-Anilino-1-naphthalenesulfonic acid ammonium salt	8.42%	Not Active
38.	Bathophenanthrolinedisulfonic acid disodium salt hydrate	7.50%	Not Active
39.	L-Ascorbic acid sodium salt	7.02%	Not Active
40.	Heptadecafluorooctanesulfonic acid tetraethyl ammonium salt	7.98%	Not Active
41.	Poly(styrenesulfonic acid sodium salt)	7.69%	Not Active
42.	Poly(4-styrenesulfonic acid-co-maleic acid)	6.59%	Not Active

	sodium salt		
43.	Poly(anetholesulfonic acid, sodium salt)	7.72%	Not Active
44.	Poly(4-styrenesulfonic acid) solution18wt% in water	7.91%	Not Active
45.	Poly(4-ammonium styrene-sulfonic acid), 30wt. % solution in water	8.58%	Not Active
46.	8-Anilino-1-naphthalenesulfonic acid ammonium salt	8.83%	Not Active
47.	3-Amino-4-hydroxybenzenesulfonic acid	8.91%	Not Active
48.	Malonic acid	7.05%	Not Active
49.	Aniline-2-sulfonic acid	5.74%	Not Active
50.	1-Naphthol-3,6-disulfonic acid disodium salt hydrate	6.87%	Not Active
51.	Hydroquinonesulfonic acid potassium salt	6.60	Not Active
52.	2,6-Naphthalenedisulfonic acid disodium salt	5.57%	Not Active
53.	Ortho-phosphoric acid	7.53%	Not Active
54.	Oxalic acid	6.60%	Not Active
55.	4-Aminotoluene-3-sulfonic acid	5.413%	Not Active
56.	Isonicotinic acid hydrazide	5.75%	Not Active
57.	5-amino-2-[(4-aminophenyl)-amino]benzenesulfonic acid	5.65%	Not Active
58.	8-Hydroxyquinoline-5-sulfonic acid monohydrate	6.08%	Not Active
59.	Anthraquinone-2-sulfonic acid sodium salt monohydrate	6.44%	Not Active
60.	L-Ascorbic acid, Free acid	6.81%	Not Active
61.	Salicyclic acid sodium salt	5.90%	Not Active
62.	Formic acid	6.66%	Not Active
62.	Ammonium bromide	9.47%	Not Active

63.	Tetra-n-butyl-ammonium bromide	6.18%	Not Active
64.	Benzyltrimethylammonium chloride	6.08%	Not Active
65.	N,N-Diethylethanolammonium chloride	8.00%	Not Active
66.	Choline Chloride	8.43%	Not Active
67.	Tetra-n-butyl-ammonium chloride	9.01%	Not Active
68.	Ammonium bromide	9.47%	Not Active
69.	Tetra-n-butyl-ammonium bromide	6.18%	Not Active
70.	Phenyltrimethylammonium chloride	5.81%	Not Active
71.	Ammonium nitrate	7.65%3	Not Active
72.	Ammonium benzoate, extra pure	5.83%	Not Active
73.	Ammonium acetate	7.88%	Not Active
74.	1-Naphthylammonium chloride	8.31%	Not Active
75.	Ammonium tungstate	5.78%	Not Active
76.	Methyltriphenyl-phosphonium bromide	5.90%	Not Active
77.	Allyltriphenylphosphonium bromide	6.78%	Not Active
78.	Isoamyltriphenyl-phosphonium bromide	6.78%	Not Active
79.	(3-Bromopropyl)triphenylphosphonium bromide	6.27%	Not Active
80.	Phenacyltriphenylphosphonium bromide	6.88%	Not Active
81.	(2-Hydroxyethyl)triphenylphosphonium bromide	6.41%	Not Active
82.	(3-Carboxypropyl)triphenyl-phosphonium bromide	6.75%	Not Active
83.	Trihexyltetradecylphosphonium bromide	5.96%	Not Active
84.	Benzyltriphenylphosphonium chloride	6.29%	Not Active
85.	Phenyltrimethylammonium chloride	5.81%	Not Active
86.	Analytical reagent grade Ammonium dihydrogen orthophosphate	5.77%	Not Active
87.	(3-Carboxypropyl)triphenyl-phosphonium bromide	6.75%	Not Active
88.	Lithium chloride	7.02%	Not Active
89.	Zinc chloride	7.00%	Not Active
90.	Iron (II) chloride tetrahydrate	6.97%	Not Active
91.	Calcium chloride dehydrate	6.66%	Not Active

92.	Cobalt chloride	6.89%	Not Active
93.	Tin (II) chloride	7.02%	Not Active
94.	Lithium nitrate	6.7%	Not Active
95.	Ammonium nitrate	6.8%	Not Active
96.	Cerium (III) nitrate hexahydrate, extra pure	6.57%	Not Active
97.	Lanthanum nitrate hexahydrate	6.69%	Not Active
98.	Bismuth (III) nitrate	5.85%	Not Active
99.	Calcium chloride dehydrate	6.66%	Not Active
100.	Cobalt chloride	6.89%	Not Active

Appendix B: Achievements during PhD study

International Awards

- **Manuchehr Eijadi Award**

  American Oil Chemists' Society (AOCS), USA 2015.
- **Honored Student Award**

  American Oil Chemists' Society (AOCS), USA 2015.
- **Young Chemical Engineer in Academia Award** (Highly Commended)

  Institution of Chemical Engineers (IChemE) Malaysia 2014.

Awards from University of Malaya

- **Bright Spark fellowship** in University of Malaya 2013.
- **University Scholarship Award** for PhD Study in University of Malaya (January 2013-August 2014).

Patents

- **(Granted Patent) 2014**

  Invention Title: ***A method for treating the high free fatty acids content in acidic plant-derived oil***

  Adeeb Hayyan, Maan Hayyan, Farouq S. Mjalli, Mohd Ali Hashim

  Grant No.: MY-150656-A, Date of Grant: 13/2/2014.

- **(Filed Patent) 2012**

  Invention Title: ***A method for producing biodiesel from crude plant-derived oil using deep eutectic solvent.***

  Adeeb Hayyan, Mohd Ali Hashim, Maan Hayyan, Farouq S. Mjalli, Inas M. AlNashef

  Filing Application No.: PI No: PI 2012700963, Filing Date: 20/11/2012.

- **(Filed Patent) 2012**

  Invention Title: ***A method for treating free fatty acids of crude plant-derived oils to obtain fatty acid alkyl esters.***

  Adeeb Hayyan, Farouq S. Mjalli, Maan Hayyan, Mohd Ali Hashim

  Filing Application No.*:* UI 2012700051, *ICP No.: C07C 51/00* Filing Date: 5/3/2012.

International Exhibitions

2014

1- **Gold Medal**, Novel deep eutectic solvents and ionic liquids for production of bio-fuel, biodiesel and glycerol from low grade palm oil. International Engineering Invention & Innovation Exhibition (i-ENVEX), 11th -13th April, 2014. University Malaysia Perlis, Malaysia.

2013

2- **Gold Medal,** Green Catalysts for Generation of Multiple Products from Low-Grade Palm Oil, Malaysia Technology Expo (MTE 2013), 21-23 February 2013. Kuala Lumpur, Malaysia.

Citation Indices (updated 15/4/2015)

- **h-index according to Google Scholar Citations is 10 and total citing articles is 330.**

- **h-index according to ISI web of knowledge is 8 and total citing articles is 122.**

Cited paper in High Journal

The following paper was cited in Chemical Reviews which is one of the most highly regarded and highest-ranked journals covering the general topic of chemistry. In 2013 Chemical Reviews has **impact factor: 45.661.**

Adeeb Hayyan, Mohd Ali Hashim, Maan Hayyan, Farouq S. Mjalli, Inas M. AlNashef. A novel ammonium based eutectic solvent for pre-treatment of low grade crude palm oil and synthesis high quality biodiesel fuel, Industrial Crops and Products, 46, (2013) 392-398. (ISI-Cited Publication/ Elsevier).

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