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Value-added Products from Palm Sludge Oil

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Abstract: The very short chain fatty acid has been recovered from palm sludge oils, a by-product of palm oil mills using vacuum distillation method. The recovered very short chain fatty acid contains mainly C6 fatty acid which is a valuable fine chemical in perfume industry. The very short chain fatty acid perfume esters were then synthesised using ethanol with sulphuric acid as catalyst. The reaction conditions were alcohol- very short chain fatty acid volume ratio of 2:1, 1.5% wt of sulphuric acid at temperature of 120°C for 20 min. The yield of very short chain fatty acid esters after distillation and purification processes was 50 to 60% wt. The treated palm sludge oils, after recovering of very short chain fatty acid was subjected to esterification using solid acid catalyst followed by conventional transesterification for biodiesel production. The free fatty acid in palm sludge oils was successfully reduced from 65% to less than 2% prior to transesterification. The conversion of free fatty acid to methyl ester and final yield of biodiesel were 98 and 83%, respectively. This paper demonstrates total utilisation of palm sludge oils by producing valuable very short chain fatty acid before converting it into biodiesel.

Key words: Palm sludge oil, esters, distillation, refining, biodiesel

INTRODUCTION

Malaysia is currently the world's largest exporter of palm oil with 16.66 million tonnes of palm oil products been exported in 2010. Among all the palm oil products, Crude Palm Oil (CPO) and refined palm oil are the most commonly traded commodities. Extraction of CPO from fresh fruit bunches requires steam for sterilisation and water for dilution which finally contribute to substantial amount of water discharged in the form of Palm Oil Mill Effluent (POME). Palm Sludge Oil (PSO) is the floating residual oil that separated during the initial stage of POME discharge to the pond. The small amount of oil that fails to be extracted and leach out from various stages of the milling process will end up in the open ponds as poor quality sludge oil. The PSO will then become the substrate for microbes that present in the natural environment. The fatty acids content in the PSO varies depending on its exposure time in the open ponds (Chow and Ho, 2002). The PSO is currently being categorised under sludge oil as it exhibits high Free Fatty Acids (FFA) and very low Deterioration of Bleachability Index (DOBI) values. Due to the inferior quality of PSO, this residual oil cannot be used directly as food source but normally being used for low-grade laundry soap formulation to substitute palm fatty acids distillate. The typical FFA content in PSO can be ranging from 40 to 80% (by weight). PSO is dark brown in colour, bad odour and solid at 25°C.

If refined, the PSO can be applied directly as boiler fuel, raw material for biodiesel production, replace 100% of palm fatty acid distillate in the soap making industry. Hayyan *et al.* (2011) and Hayyan *et al.* (2010) investigated the production of biodiesel from PSO using conventional method including esterification process in order to reduce high FFA content in PSO via acid catalyst followed by transesterification process to produce biodiesel. Chow and Ho (2002) studied on the chemical compositions of oil droplets in the PSO and reported that the composition of the major lipids of PSO is similar to that of commercial palm oil. Huang *et al.* (2010) studied the production of biosurfactant from the PSO. The relatively high concentration of such biosurfactant in the oil droplets may have commercial potential as a value-added resource from the palm oil mill.

This study aimed to recover very short chain fatty acid (VSCFA) from PSO. The process includes producing VSCFA from PSO via degumming, discolourisation and vacuum distillation. Strong bleaching agents such as hydrogen peroxide and sodium hypochlorite are added to discolourise the PSO. The VSCFA was reacted with selected alcohols in the presence of sulphuric acid. The treated PSO was also esterified and transesterified for the production of biodiesel. The fuel properties of PSO biodiesel were analysed and discussed.

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MATERIALS AND METHODS

Materials: The PSO was collected from a Tennamaram palm oil mill, Selangor, Malaysia. The PSO was made up of 65% FFA with remaining elements consist of triglycerides and traces of impurities. Analytical grade methanol (98%), ethanol and sodium hydroxide were purchased from Merck KGaA, Darmstadt, Germany. Phosphoric acid was purchased from Merck KGaA, Darmstadt, Germany; hydrogen peroxide (30%) and sodium hypochlorite (10% with chlorine) and para-toluene sulfonic acid (ρTSA) were purchased from R and M Chemicals, Essex, United Kingdom.

Recovery of very short chain fatty acids from palm sludge oil: About 300 g of PSO was weighed accurately in a three-neck round flask. The PSO was heated under nitrogen blanketing to 90°C. Degumming step was carried out by adding 0.5 wt.% phosphoric acid (20% in aqueous) into PSO at 90°C and stirred for 10 min. Accurately 1.0 wt.% of strong bleaching agents e.g. hydrogen peroxide and sodium hypochlorite was added after 10 min of reaction, subsequently raising the reaction temperature to 105°C and hold for 15 min. The mixture was then filtrated under vacuum. The filtered oil was transferred into another two-neck round flask. Anti-bumping granules were added to the mixture and subjected to vacuum distillation step at temperature of 240°C under vacuum for 20 min. The VSFCA was collected as distillate and analysed using GC-FID. The treated PSO was further processed into biodiesel.

Synthesis of VSCFA esters: Approximately 100 g of VSCFA and 50 mL of ethanol were mixed in the presence of 3 mL of concentrated sulphuric acid in a two-neck round bottom flask. The two-neck round bottom flask was immersed into hot oil bath at 120°C for 20 min. Water was added to the mixture after reaction to wash out excess ethanol and sulphuric acid. The esters layer was subjected to steam distillation by bubbling steam into the mixture under vacuum. The perfume ester was collected in the steam condensate and dried using drying agent e.g. sodium sulphate anhydrous. A total of 60 g of perfume esters with fruity smell was collected and analysed.

Production of palm sludge oil biodiesel : About 500 g of treated PSO with FFA content of 65% was weighed accurately into two-neck flask. Catalyst was prepared by dissolving 5 g of ρTSA in 120 g of methanol based on molar ratio of methanol and treated PSO of 1:1. The ρTSA solution was added into PSO and reacted at 65°C for 60 min under atmospheric condition with magnetic stirring. The reaction mixture was poured into a separating funnel and allowed to settle into two layers. The bottom layer was decanted and sample was taken from top layer to determine its FFA content. The top layer was subjected to second step esterification by adding 0.35 wt.% of ρTSA (based on feed) into 53 g of methanol (based on molar ratio of 1:1 of methanol and FFA of feed). The bottom layer was drained after the reaction followed by water neutralisation and removal of water from the top layer thereafter. The esterified PSO was further transesterified using 0.5 wt.% of NaOH in methanolic solution (based on molar ratio of methanol and esterified PSO of 4:1) at 65°C for 60 min. Bottom layer was decanted and the reaction mixture was purified by water washing and drying. The final PSO biodiesel produced was then analysed for its critical parameters based on EN 14214:2003 specifications.

Analytical method: The ester content, monoacylglycerols (MG), diacylglycerols (DG), triacylglycerols (TG) was analyzed using GC-FID (Hewlett-Packard 5890 Series II, Palo Alto, CA) according to modified method by Harrison *et al*. (2007). The Fatty Acid Composition (FAC) was determined using PerkinElmer GC-FID (AutoSystem XL, Shelton, CT) according to modified method by Harrison *et al*. (2007).

RESULTS AND DISCUSSION

Composition of very short chain fatty acids: VSCFA has been successfully recovered from PSO as distillate in the deodorisation process of PSO. A total of 150 g of VSCFA was collected from 500 g of crude PSO. The fatty acid compositions of VSCFA were shown in Table 1. The distillate was found to contain 95 wt.% of VSCFA ranging from carbon 2 to 6. Conventionally, VSCFA has been widely used as raw material in the fragrant industry for the production of perfume via esterification process. VSCFA such as acetic and propionic acids are produced during fermentation of dietary fiber and have shown to inhibit HMG-CoA reductase, an enzyme involved in the production of cholesterol by the liver (Demigne *et al*., 1995). Caproic acid is not only used in the formation of esters but also commonly used as artificial compound in production of butter, milk, cream, strawberry and other

Table 1: Fatty acid compositions of very short chain fatty acid (VSCFA) recovered from palm sludge oil

Type of fatty acid	Percentage (wt.%)
C2-C5	15
C6	80
C8	2
C10	2
C12	1

Table 2: Composition of very short chain fatty acid (VSCFA) esters produced from palm sludge oil distillate via esterification process

Ester	Chemical formula	Flavour/Odour
Ethyl acetate	$C_4H_8O_2$	Pear, orange, banana
Ethyl butanoate	$C_6H_{12}O_2$	Pineapple, banana
Ethyl caproate	$C_8H_{16}O_2$	Pineapple, banana
Ethyl caprylate	$C_{10}H_{20}O_2$	Apricot, pear, pineapple
Ethyl caprate	$C_{12}H_{24}O_2$	Grape, pear
Ethyl laurate	$C_{14}H_{28}O_2$	Peach, pear

Table 3: Two-stage esterification process of treated PSO using pTSA as catalyst

Sample	Free fatty acid content (%)
Starting PSO	65.00
PSO after 1st step esterification	12.71
PSO after 2nd step esterification	1.65

flavours. Therefore, the recovered VSCFA has vast potential to convert into downstream value-added products.

Synthesis of perfume esters from very short chain fatty acids: The synthesis of VSCFA perfume ester via esterification process by addition of ethanol has been carried out using sulphuric acid as catalyst. Table 2 shows the type of esters formed in the reaction which gives typical fruity smell of the ester. The VSCFA esters produced were light yellowish in colour comprising of ethyl acetate, ethyl butanoate, ethyl caproate, ethyl caprylate, ethyl caprate and ethyl laurate. The type of fruity smell and flavour varies depending on the percentage of fatty acid in the VSCFA.

Production of biodiesel from treated palm sludge oil: To further value-add to the entire process, the treated PSO was esterified and transesterified for the production of biodiesel using pTSA and caustic soda as catalyst, respectively. Esterification process was used in order to pretreat the SPO by converting the high content of FFA to fatty acid methyl ester using acid catalyst. The initial content of FFA in SPO applied in this study which would not favorable for biodiesel production indicated that transesterification process will not occur if the FFA content in oil feedstock is more than 3%. Table 3 depicts the reduction of FFA in PSO by esterification process using pTSA. The results showed that two steps esterification reactions were sufficient to reduce FFA from 65 to 1.65%. Total reduction in the content of FFA was 97.4% after two steps of esterification process. Table 4 shows the properties of PSO biodiesel benchmark on the European Standard Specification EN 14214:2003 for biodiesel. The findings showed that the biodiesel produced under the optimum conditions meets the minimum specifications of fatty acids alkyl esters as stipulated in EN 14214:2003. The high ester content of PSO biodiesel of 97.71% was achieved basically attributed by employing a proper pre-treatment process on PSO before esterification and transesterification reactions. The fatty acid composition of PSO biodiesel was determined and results were shown Table 5. It was found that the PSO biodiesel contains higher amount of saturated fatty acid with methyl palmitate and methyl stearate of 49.1 and 3.76 wt.%, respectively.

Table 4: Fuel properties of PSO biodiesel

Property	PSO biodiesel	EN 14214:2003
Ester content (% mM^{-1})	97.91	96.5 (min.)
Density at 15°C (kg m^{-3})	877	860-900
Oxidation stability at 110°C (h)	8.74	6 (min.)
Water content (mg kg^{-1})	130	500 (max.)
Acid value (mg KOH g^{-1})	0.35	0.50 (max.)
Flash point °C	180	120 (min.)
Cloud point °C	9.9	-
Pour point°C	12.9	-
Monoglyceride content (% mM^{-1})	0.08	0.8 (max.)
Diglyceride content (% mM^{-1})	0.03	0.2 (max.)
Triglyceride content (% mM^{-1})	0	0.2 (max.)

Table 5: Composition of fatty acid methyl esters of palm sludge oil biodiesel

Fatty acids	Fatty acid compositions (wt.%)
Lauric acid methyl ester	0.42
Myristic acid methyl ester	0.82
Palmitic acid methyl ester	49.11
Stearic acid methyl ester	3.76
Oleic acid methyl ester	36.93
Linoleic acid methyl ester	8.31
Alpha-linolenic acid methyl ester	0.65

CONCLUSIONS

The study revealed alternative processes for value addition of PSO which is a by-product from palm oil mills. The VSCFA has been successfully produced from PSO and further synthesised into ethyl esters or better known as perfume esters. The results indicate that different combinations of alcohols and VSCFA could produce VSCFA esters with dedicated fragrant at highest yield of 60 wt.% based on the feed. The result also indicates that the treated SPO can be an alternative and economical feedstock for biodiesel production. It was found that the two-stage of esterification process was sufficient to reduce the FFA content from 65 to 1.65% with pTSA as catalyst. The highest yield of biodiesel obtained after transesterification process was 86% with ester content of 97.91%. This study provides a new dimension on the value-addition and utilisation of by-product from palm oil mills for the production of VSCFA cum biodiesel.

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