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Residual crude palm oil resources and recovery method: A Review

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Abstract
Over the past few years, Malaysia is among countries who led the world's crude palm oil (CPO) production. This scenario however giving drawbacks due to a large volume of biomass in the form of oil palm empty fruit bunches (OPEFB), oil palm mesocarp fiber (OPMS), decanter cake (DC) and palm oil mill effluent (POME). Whilst they still contain valuable residual oil, which currently million tons of these biomass treated as solid and liquid waste. As opposed to the elimination approach, this review paper is aimed to give an overview on the residual crude palm oil recovery method from different types of biomass resources. Common method proposed in the industry is by extraction using an organic solvent such as n-hexane, but due to it classified as hazardous to air pollutant and highly flammable, many researchers tried to find better approaches such as green solvent D-limonene, sub-critical water, and supercritical CO_2 with or without ethanol. Apart from that, some of the researchers recovered the residual oil by physical means such as pressing, hydro solvent-assisted steam extraction (HYSASE), high pressure water spray (HPWS) and nanofiber absorption technique. For the time being, most of the researchers focused on the oil recovery for a specific type of biomass, but by understanding the method principle, it could bring possibility to treat another type of biomass or can be combined to get high yield of residual oil. Therefore, this strategy will pave the way for several potentials in residual oil utilization such as biodiesel, bio-lubricant, MAG and DAG productions.

Keywords: Residual crude palm oil, recovery method, POME, EFB, palm oil biomass

Introduction

Malaysia popularity in producing crude palm oil (CPO) cannot be debated indeed. Malaysia becomes second world's largest producer and exporter after Indonesia. 19 million tons of CPO produced by Malaysia in 2019 (MPOB 2019a).

The oil palm industry is a land intensive industry where the planted palm oil land area approximately 5.58 million hectares in 2019 (MPOB 2019b). Rather than new forest land explorations that lead to disturbance of the forest systems, loss of animal's habitats and pesticide pollutions in maintaining the plantation, the CPO industries has diverted its efforts to increase oil production by operating at optimum process conditions. One way to achieve this goal is by increasing the oil extraction rate (OER). OER has been used to evaluate the performance of mill by comparing the ratio of palm oil produced with the total fresh fruit bunch (FFB) processed per day (Hussain et al., 2003). The standard OER for Malaysian palm oil industry's is around 20%, which is about 0.2 ton of CPO per ton of FFB (Chung et al., 2017). However, according to the Palm Oil National Key Economic Area (Pemandu 2019), under the Entry Point Project 4, the expectation for Malaysia is to increase its OER up to 23% by 2020. Recovering the residual oil from palm oil wastes is one of strategies on increasing the OER to meet the government target.

The utilization of residual oil highly depends on its quality, either for edible or non-edible purposes. The quality of residual oil also depends on the method used in the recovery process. Residual oil that meets the standard requirement of CPO can be used for any edible purpose. Further analysis of residual oil is necessary to identify the potential use of residual oil such as in biodiesel, soap making, polymer, bio lubricant, monoacylglycerols (MAG) and diacylglycerols (DAG) productions. Turning the residual oil to beneficial product could bring extra side income to the mill.

Source of oil loss

The oil recovered in the mill process (OER), should not identified on its own but it is the outcome of total oil coming to the mill minus the total oil loss. The percentage of oil loss in palm oil mill were highlighted by Walat et al. (2013), indicating that the total oil loss about 1.93%.

Table 1: Percentage of oil loss during different stages of milling process (Walat et al, 2013).

Source of oil loss	Oil loss on Fresh fruit bunch (FFB) %
Steriliser condensate	0.16
EFB	0.56
Fruit loss in EFB	0.03
Unstripped bunches	0.02
OPMS	0.55
Nuts	0.06
Sludge/decanter	0.46
Washings/Spillages	0.09
Total oil losses	1.93
OER	20.8
Total oil (20.8+1.93)	22.73
Oil milling efficiency (20.8/22.73) × 100	92

Conventional method for residual oil recovery

The conventional method for residual oil recovery is by using solvent extraction or Soxhlet extraction method. It is widely used for oil recovery compared to other type of recovery methods.n-Hexane is commonly used in oil recovery method; however, it suffers several major drawbacks; highly flammable, non-renewable sources, and classified as hazardous air pollutants that can cause harmful effect on environment and on human health.

1. ***Solvent extraction***

Solvent extraction is the isolation of a substances or components from solid or liquid by using a solvent. Solubility, hydrophobicity or hydrophilicity, molecular weight, vapor pressure, and acid dissociation are the fundamental properties of substance that use for the selection of extraction solvent (Wells, 2003). Usually solvent to waste ratio can be increased or multiple extraction stages can be done to improve the process efficiency.

To study the extraction of residual oil from POME by organic solvent, Ahmad et al. (2003) used six different types of solvent; n-hexane, pentane, benzene, petroleum ether, and petroleum benzene. The effect of solvent ratio, mixing speed, mixing time, and pH were analyzed to determine the optimum conditions for the extraction. The results show that n-hexane is the best organic solvent to extract oil and grease from POME followed by benzene, petroleum benzene, petroleum ether, pentane and n-heptane. It was estimated around 0.54 g of oil and grease per liter POME can be extracted at optimum conditions; solvent to POME ratio 6:10, 200 rpm mixing speed, 20-minute mixing time and at pH 9.

2. ***Soxhlet extraction method***

Soxhlet system process start with the vaporized solvent passes through the side arm, condenses in the condenser and then floods in the thimble. Extraction occurs when the solvent interacts with the oil source in the thimble and the solvent with substance drains into the flask through the siphon device (Kou et al., 2003).

Fauzi et al. (2016) studied on the extraction of oil from filter cake sludge using Soxhlet extraction where three different solvents were used; n-hexane, methanol and acetone. After the sludge collected from International Foodstuffs Co (IFFCO) Malaysia, it dried for 6 days in the oven at 105^{o}C, until the weight of the sample become constant. Drying before extraction helps to rupture the matrix walls, thus it prepares the solvent to dissolve with the oil. The highest percentage of oil yield was extracted using methanol, which yielded 66.6% (by weight) followed by n-hexane 33.3%, and acetone 13.3%. This is because methanol is the most polar solvent, so it is more likely to extract most of the polar compounds from the matrix of the material. The methanol extraction from this study, had showed a greater concentration of esters (35.8%), indicating that the extraction involved esterification reaction and the extract could be further used for biodiesel production.

Recovery method for different types of biomass

At the time being, the innovation of residual oil recovery method was created for specific type of biomass.

Table 2: Summary of different method of residual oil recovery for different type of biomass.

Biomass	Recovery Method
POME	-Nanofiber absorption followed by manual pressing, (Chung et al, 2017).
EFB	-Extraction using Sub-critical water, (Kurnin et al, 2016) -Steam injection, (Gomez et al, 2014) -Mechanical Extraction; Pressing, (Jogersen, 1985). -Pressurized hot water, (Yunos et al, 2016)
OPMS	-Supercritical CO_2 extraction, (Nang et al, 2006).
DC	-Green Solvent; D-Limonene (Sahad et al, 2015).

1) ***Palm oil mill effluent (POME)***

POME is the effluent that generated from EFB sterilization and CPO clarification in the palm oil mill. According to Mohammad et al. (2008), it is a colloidal suspension that consist of several composition such as 95 - 96% water, 0.6 - 0.7% oil and 4 - 5% total solids including 2 - 4% suspended solids. There is a large portion of emulsified oil that had polluted the POME and the oil which in emulsified form cannot be separated by gravity separation. The treatment system is usually a combination of anaerobic and aerobic ponds. The residual oil in the effluent is approximately 4000 - 6000 mg/L, while the regulatory threshold value for oil and grease is 50 mg/L (Ahmad et al., 2005).

Chung et al. (2017) focused on the recovery of residual oil from POME by using polypropylene nanofiber (PP NF) in which the field trial had been conducted in palm oil mill. The PP NF was produced using melt-blown technique. It was melted and blew through a very thin nozzle and elongated into nano fibers. The NF was submerged in the sludge pit where the sterilizer condensate and sludge clarification mixed to form POME before passing to the cooling pond. The residual oil was desorbed by pressing with manual roller within the temperature range of 60 - 70^{o}C. The pressed NF was then tested using both solvent extraction and Soxhlet analysis while the pressed liquid from the NF comprises of water, oil and sludge, was brought to manual skimming to obtain the residual oil. The process recovered 12.19 g of oil/g NF from ~1070-ton POME for 34h of the mill production time. The oil holding capacity for NF was around 1.06 to 1.29 g oil/ g NF after the field test. The oil holding capacity indicated the ease of oil to desorb from the NF. The NF also remained effective after 4 rounds of reuse, which proven by GC-FID study of the recovered oil, indicating no trace of polypropylene contamination.

2) Empty fruit bunch (EFB)

The EFB is generated after the stripping process in which after sterilization, the fruits are separated from the stalks. According to Baharuddin et al. (2009), EFB can be used as a wood composite, fiberboard, soil mulching material, and composting. EFB comprised of about 20% cellulose, 23.9 - 25.1% hemicellulose, 23.5% lignin and 7.4% oil. The oil was previously transferred to EFB surface due to mechanical pressure imposed during the FFB conveying (movement) and threshing process, as well as due to increased contact time; prolonged sterilization and long delays between sterilizing and stripping (Majid et al., 2012).

According to Kronholm et al. (2007), sub-critical water (sub-cw) is defined as liquid water that lies under high temperature (between atmospheric boiling point to less than its critical temperature (374ºC)) and high-pressure condition to keep water in liquid state. The dielectric constant of water reduces from 78.5 at room temperature up to 29 at 250ºC, which make it behaves almost like ethanol to extract the oil. Kurnin et al. (2016) studied on the recovery of residual palm oil and valuable material from EFB by using sub-cw. The spikelet was treated with sub-cw in the temperature range 180 - 240ºC and the holding time of 2 - 5 minutes. The highest yield of oil was 0.075g-oil/g-dry EFB. The yield of oil strongly depends on the temperature and time; however, too high temperature can cause oil degradation (> 240ºC). The oil extracted through this method was comparable (84.5%) to that obtained oil by n-hexane-Soxhlet method. The oil that produced using sub-cw contained FFA between 3 - 12%, because of increment in temperature encouraged the FFA formation by hydrolysis of triglyceride at temperature >240ºC which also supported by (Kronholm et al, 2007 and Alenezi et al, 2008). This experiment also produce sugar (yield 0.20g-sugar/g-dry EFB) from hydrolysis of hemicellulose and cellulose which also supported by (Carrier et al., 2012 and Cocero et al., 2018) and tar from pyrolysis supported by (Ariffin et al, 2008).

Recovery of residual oil for palm oil using steam injection also gains attention lately as it already applied in petroleum industry for oil recovery. Gomez et al. (2014) used the combination of water and steam process to recover the residual oil from EFB. The proposed process was called as hydro solvent-assisted steam extraction (HYSASE). The spikelet was firstly loaded into the chamber and water was added until the spikelet was fully submerged. After that, the saturated steam was injected through the valve. This allowed the steam to bubble (provide agitation) and heat the water until 100ºC. Finally, the water and oil were drained out and further separated using hexane for oil content analysis. The overall process resulted in 83% residual oil removal from the spikelet due to reduction of oil viscosity (which brings the oil viscosity close to water viscosity) and creation of macro-turbulence by bubbling the water increased the interparticle collisions and penetration of micropores within the biomass which also support by (Vilkhu et al., 2008). However, the residual oil properties have high free fatty acids (FFA) due to hydrolysis of triglycerides occurred during the process due to high temperature and high water to oil ratio. The residual oil also reported to have poor bleachability index (DOBI) and peroxide value (PV) compared to the oil before going through the process. Monoglycerides and diglyceride produced through this method affecting the emulsification of oil and water as they are high hydrophilicity due to OH functional group which also support by (Gaonkar 1989).

Residual oil was traditionally recovered by using mechanical means. Jogersen. (1985) suggested to recover the residual oil by pressing the EFB. The bunches were splited longitudinally and were then passed into large single worm screw press for dewatering and removal of residual oil. The average oil recovery from EFB was minimum of 1.5%. The resultant fibrous material served as valuable fuel for steam generation. However, using this method, some portion of residual oil adsorbed to the inner layer of spikelet, and oil would not be fully recovered.

Yunos et al. (2016) studied on oil recovery using pretreatment with compressed water and steam to consider minimal damage of the lignocellulosic material. The method of using high pressure water system (HPWS) was developed to recover the residual oil that entrapped on the surface of EFB. The system consisted of high-pressure cleaner and vessel. The results show that, the highest residual oil recovery yield is 94.41 wt.% at 150ºC. As the temperature increased from 30 to 150ºC, the oil removal rate also increased since elevated temperature is capable in lowering the oil viscosity, thus increased the oil diffusion and solubility. The FFA, PV and DOBI of the residual oil show poor quality after using HPWS process. The DOBI decreases with the temperature increments due to carotene is broken down to secondary products which also supported by (Bonnie, 1999). Despite the low quality of residual oil produce using HPWS method, it complies with EN 14214 international biodiesel fuel standard thus suitable to use as biodiesel feedstock. The remaining EFB shows the increment of surface area, pore volume, cellulose and less lignin content thus suitable to be used as beneficial feedstock for value-added product such as ligno-ethanol.

3) Oil palm pressed mesocarp fiber (OPMS)

OPMS is a residue remains after extraction of oil from fresh fruit, which contains about 5 - 6% residual oil and minor components such as carotenoids, tocopherols, tocotrienols, phytosterols, and squalene (Choo et al., 1996). Usually, the mesocarp fiber was burned for electricity generator, along with palm kernel shells, which resulting in loss of much valuable oil and nutrients.

Nang et al. (2006) studied on the extraction of residual oil from OPMS by using supercritical CO_2 (SC-CO_2) with and without ethanol. CO_2 is often considered the preferable solvent compared to hexane because of its nontoxic, non-flammable, and environmentally friendly properties. The results show that, by using SC-CO_2, 0.054 g oil per g of dried fiber was recovered. Total SC-CO_2 residual oil recovery was 93.l%. The dried fiber produces higher yield compared to the fresh fiber due to the presence of moisture that can influence the phase characteristics of SC-CO_2. However, oxidative stability of fresh fiber is higher compared to the dried fiber. The polarity and solvating power of SC-CO_2 were increased when ethanol was added.

4) Decanter cake (DC)

Decanter is used to treat the underflow of clarification tank by separating the remaining oil from the solid. During the process, the fibrous solid trapped and absorbed the oil before discharging as OPDC (Sahad et al, 2015). Nowadays, most of the palm oil mills use OPDC as animal feed and fertilizer (oil palm plantation) due to its high nutrient content.

As part of searching for green solvent, the popularity of D-limonene also increased. It is one type of terpene, where this bio-solvent derived from citrus fruit through steam distillation. It is better than hexane due to its advantages of low toxicity, highly recyclable, low viscosity, low cost and high boiling point (175ºC) (Liu et al. 2004). Sahad et al. (2015) performed the extraction of residual oil from OPDC using D-limonene. As a result, D-limonene was able to recover 100% of the residual oil. D-limonene is slightly polar than n-hexane, therefore it attributed to higher dissolving power to triglycerides (Chemat et al., 2012). The high boiling point during extraction also could enhance the desorption rate of oil from OPDC due to lower viscosity. However, the quality of residual oil reduced due to deterioration shown high FFA and low DOBI.

Conclusion:

Biomass such as POME, EFB, OPMS and DC shows great potential as residual oil resources. Apart from using organic solvent, all the proposed methods (PP NF absorption, Sub-CW, SC-CO_2, HPWS, HYSAE, D-Limonene) can remove or recover the residual oil comparable to conventional method. Some of the method exposed the biomass toward high temperature and moisture, thus accelerated the rate of oil degradation reaction, which affect the residual oil quality such as PV, DOBI and FFA content.

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