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Purifying the Used Palm Olein with the Durian-Peel Activated Carbon

Asriana Ibrahim[1,2,*], Muhammad Adib Fadzil[1]

[1] Fakulti Teknologi dan Kejuruteraan Mekanikal, Universiti Teknikal Malaysia Melaka (UTeM), Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia
[2] Centre for Advanced Research on Energy, Universiti Teknikal Malaysia Melaka (UTeM), Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia

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ABSTRACT

Used Palm Olein (UPO) is generated from the deep-frying process during meal preparation when exposed to high heating temperatures for an extended period. Repeated use of UPO can cause damage to its chemical content due to oxidation reactions in such a way that the colour becomes darker. At the same time, it also produces volatile compounds that can cause carcinogenic effects on humans. This study investigated the potential of the durian-peel activated carbon (DPAC) in enhancing the three physicochemical properties of the UPO, i.e., colour, free fatty acids (FFAs), and peroxide value. The effect of contact time and volume ratio on producing DPAC was also investigated. The higher the contact time and volume ratio, the better the UPO. At the best parameter of 1: 0.1 volume ratio and 60-minute contact time, the FFA content of UPO was reduced by 20.1% and the peroxide value by 9.3%. Keywords: Activated carbon, durian peel, palm olein, purification

1. Introduction

Palm olein (PO) is the liquid fraction of palm oil in cooking oil, and it dry-heats the foods via convection. Thus, it is a heat-transfer medium, particularly in deep-frying. In Malaysia, 45 million kg of POs are consumed monthly [1]. Restaurants, hotels, and fast-food outlets regularly produce large quantities of used palm olein (UPO). However, repeated uses of PO destroy its chemical structures due to oxidation, making its colour darker while increasing its viscosity and density due to the formation of undesired components from oxidation, polymerisation, and hydrolysis [2]. Besides, volatile organic compounds, particularly aldehydes [3], produced during chemical reactions of using UPOs repeatedly may cause a carcinogenic effect on the human, such as increased tumor proliferation [4].

Meanwhile, dumping untreated UPOs into waterways pollutes the aquatic ecosystem, threatening freshwater and marine biota, and disrupts the natural food chain [5]. Terrestrial disposal of UPOs produces volatile substances into the air while dumping them into sewage pipelines forms

* *Corresponding author.*
E-mail address: asriana@utem.edu.my

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fatbergs and clogs the system. Therefore, recycling UPO has been initiated to mitigate issues related to its disposal. There are two techniques for recycling UPOs: chemical and physical treatment [6]. Although these techniques resolve the problem of waste pollution indirectly, the issue of organic waste flooding landfills remains serious in Malaysia as it generates the highest quantity of waste [7]. In particular, during fruit seasons, littered peel wastes substantially increase the quantity of waste for landfills, while causing odour pollution and aesthetic problems.

In Malaysia, studies investigating the durian-peel activated carbon (DPAC) for mitigating pollution remain scarce, particularly on the effectiveness of purification based on the volume ratio of DPAC to UPO. Therefore, this study used DPAC to purify UPO at different volume ratios and contact times. Base treatment was used to enhance the carbon for pollutant adsorption. The outcome of this study might encourage green technology for waste management while promoting environmental sustainability.

2. Literature Review

Landfills containing decaying organic waste are partially responsible for climate change by producing a higher amount of atmospheric methane, accounting for 7% of global greenhouse gas emissions [8]. In Malaysia, organic scrap is the most generated waste at 16,688 tons per day [9]. Developing a culture of reducing waste should be encouraged to curb this growing problem. The Malaysian society must understand the global agenda and support development that balances economic growth and environmental sustainability. The aim is to achieve the Sustainable Development Goal (Target 12.5) of the United Nations to significantly reduce waste generation through prevention, reduction, recycling, and reuse by 2030. In this respect, industrial symbiosis is an appropriate approach for reducing organic wastes by transforming them into raw materials for another industrial application [10]. For example, UPO is used as a raw material for biodiesel production. Specifically, fruit-peel waste is used as activated carbon, i.e., a purifying agent, to recycle the UPO.

Numerous studies investigated the use of activated carbons from organic wastes as an adsorbent to purify UPO. Botahala *et al.,* [11] found that activated carbon from candlenut shell effectively purified used cooking oil with a 66% reduction of peroxide value compared to the 59% of rice husk. Another study examined the quality of used cooking oil using synthesised activated carbon from coconut fibre with an activator medium of phosphoric acid to reduce the free fatty acid (FFA) by 93% [12]. Also, Zulkifli *et al.,* [13] investigated the effect of activated carbon made from banana peel particle size for the removal of UPO. They found that the particle size of 140 meshes and an absorption time of six hours reduced FFA by as much as 78%.

Activated carbons are widely used for adsorbing gaseous- and liquid-phase pollutants. A study proved that activated carbon from banana peel show good capabilities to adsorb carbon monoxide gas emission from motor vehicles up to 44% [14]. Another study found that the coal spills based activated carbon by physical activation show good copper ion adsorption in water treatment [15]. Some applications use these carbon adsorbents because of their characteristics and surface area. The high surface area, large porosity, well-developed internal pore structure, and a functional group on the activated carbon surface make it a valuable material for various applications. The adsorption of impurity using carbon adsorbents relies on the forces between solid-liquid molecules, such as hydrophobic interactions, Van der Waals forces, hydrogen bonds, π-π interaction, π complexation, and electrostatic interaction [16].

Meanwhile, durian (Durio zibethinus Murr) is a seasonal tropical fruit cultivated abundantly in Malaysia. There are two fruiting seasons annually: one in June and another in December, during

which durian peels generate a substantial quantity of organic waste. Chemically, durian peels contain 47.2% cellulose, 9.6% hemicellulose, 9.9% lignin, and 4.2% ash [17]. Therefore, durian peel is an adequate raw material for producing activated carbon since it contains Lignocellulose. The activated carbon of durian peel was first used to remove methylene blue from aqueous solutions [18]. Besides, the durian peel surface possessed some carbonyl and hydroxyl groups, probably contributing to the high efficiency of dye removal in wastewater treatment [19].

During the carbonisation and chemical activation, the polymer structure of these chemical components is decomposed, releasing most of the non-carbon elements from the carbon framework. In the chemical activation, the acid treatment would generate more pores on the surface of durian peels to enhance the capacity of removing pollutants [20]. This acid treatment might change the morphological structure and elemental composition of the durian peel surface, increasing the proportion of carbon for pollutant adsorption. Besides, sulfuric acid reduced the activation temperature and increased the specific surface area by forming the activated carbon microporous structure for expanding the carbonyl and sulfonyl groups [21]. However, the acidic solution used in these studies was a carcinogen. Another study using base (potassium hydroxide or KOH) treatment for preparing activated carbon from durian peel revealed that the activated carbon posed a high Brunauer-Emmett-Teller (BET) surface area [22].

Recently, DPAC was used to adsorb impurities in used cooking oil and it reduced FFA and peroxide values while yielding the best density of used oil [23]. When investigating the effect of carbonisation temperature in lowering the acid number and peroxide value of used cooking oil, Sari *et al.,* [24] found that at 600 °C, DPAC reduced the acid number by 87.7% and peroxide value by 69.5% via base-chemical activation.

3. Materials and Methods

3.1 The Preparation of Activated Carbon

This study used durian peels collected from local markets in Melaka, Malaysia, in June 2022. Peels were washed several times using distilled water to remove dirt and impurities and cut into small pieces. They were dried under direct sunlight for three days at approximately eight hours per day at an average temperature of 31°C and humidity of 66%. The dried peels were then carbonised for two hours at 400 °C in a furnace (Model: Carbolite Elf 11/14B, England), cooled to room temperature, and crushed using a mortar and pestle. The carbonised peels were chemically activated by soaking them in 0.5 M KOH (Classic Chemicals, Malaysia) for 24 hours. This DPAC stock was washed using distilled water until pH 7, filtered with a nylon filter cloth, and dried at 100 °C in an oven (Model: Memmert UM200, Germany) for two hours. The DPAC stock was mashed and sifted to yield a uniform particle size between 0.3 to 0.355 mm using the USA Standard Test Sieve ASTM E11 numbers 45 and 50. This DPAC stock was stored in a desiccator for further analysis. Figure 1 shows the flow for the preparation of DPAC.

3.2c Purification of UPOs

UPO samples were collected from local deep-fried chicken stalls around Krubong of Melaka. UPO and DPAC samples were mixed at varying volume ratios (in unit gram), i.e., 1: 0.2, 1: 0.1, 1: 0.05, and 1: 0.025, and stirred at room temperature with several contact times of 15, 30, 45, and 60 minutes. The purified UPO was then filtered with filter paper (Brand Smith A0332) and analysed for three components; colour, free fatty acids, and peroxide value. Results were compared with the quality requirements of refined, bleached, and deodorised PO products listed in the MS 816 (Table 1) [25].

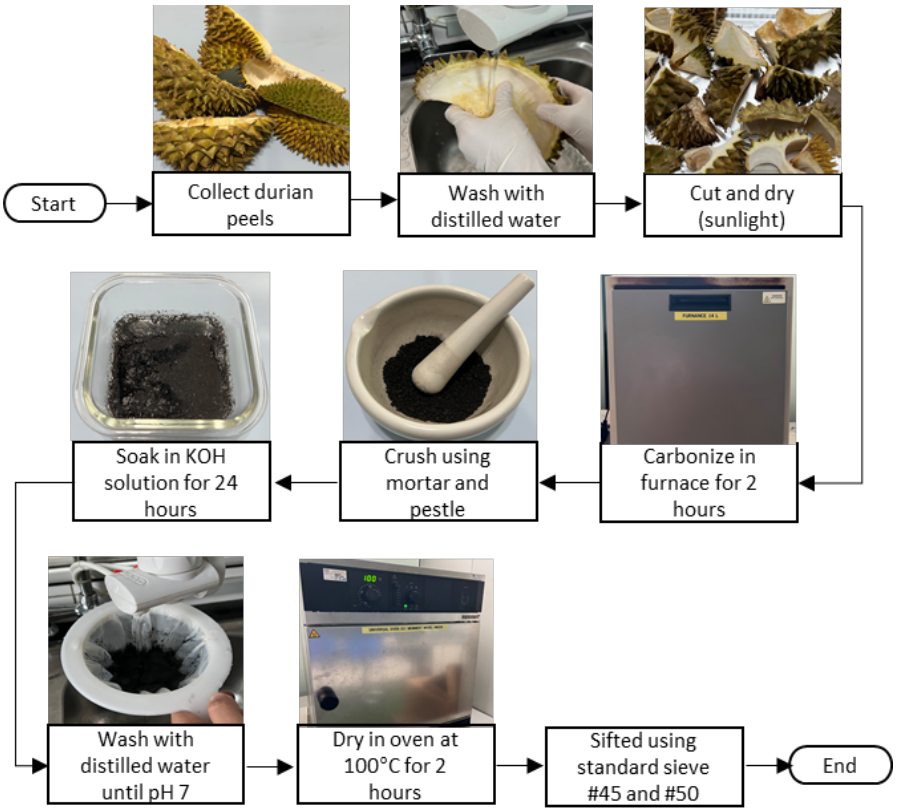

Fig. 1. The flow of preparing the durian-peel activated carbon (DPAC)

Table 1
Quality requirements for palm olein products [25]

Characteristics	Products requirements			
	Crude	Neutralised	Neutralised, bleached	Refined, bleached and deodorised/neutralized, bleached and deodorised
Free fatty acid (as palmitic), % max	5.0	0.25	0.25	0.10
Moisture and impurities, % max	0.25	0.10	0.10	0.10
Iodine value (Wijs), min.	56	56	56	56
Slip melting point, °C max.	24	24	24	24
Peroxide value, meq O_2/kg, max.	-	-	-	2.0
Colour, 133.35 mm (5 1/4 in) Lovibond, max.	-	-	20R	3R

4. Results and Discussion

Figure 2 shows the colour differences among samples of used, purified, and virgin POs. Table 2 shows the Lovibond scale for the identified colours [26]. The turbidity of UPO was attributable to impurities from the reaction of brown pigments in fried foods, causing oxidation and polymerisation of unsaturated fatty acids during the frying [27]. The results show that DPAC could clear the turbidity by absorbing impurities while changing the UPO colour.

Table 2
Colours identified using the Lovibond scale

Type of oil	Lovibond scale
Used Palm Olein (UPO)	13
Purified UPO using DPAC	7
Virgin Palm Olein	3

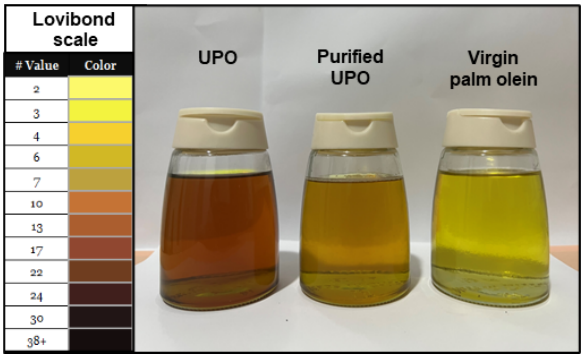

Fig. 2. Colour determination using Lovibond scale

Figure 3 shows the FFA plot against the contact time with 0.17% FFA for UPO at the non-contact time (0 minutes). At the longest contact time, i.e., 60 minutes, FFA values were reduced by 16.6%, 17.8%, 20.1%, and 20.1% for the volume ratios of 1: 0.025, 1: 0.05, 1: 0.1, and 1: 0.2, respectively, approaching the reference value at higher volume ratios. The adsorbent surface increased with the volume ratio, allowing more space to adsorb impurities. Meanwhile, a higher contact time would provide more contact between the adsorbent and impurities. These two conditions enhanced the absorption of fatty acids in the oil by DPAC. However, the relative rate of reduction for all volume ratios was approximately 0.001 throughout the longest contact time. A nearly smooth gradient suggested that the relative rate of reduction was the same regardless of the volume ratio

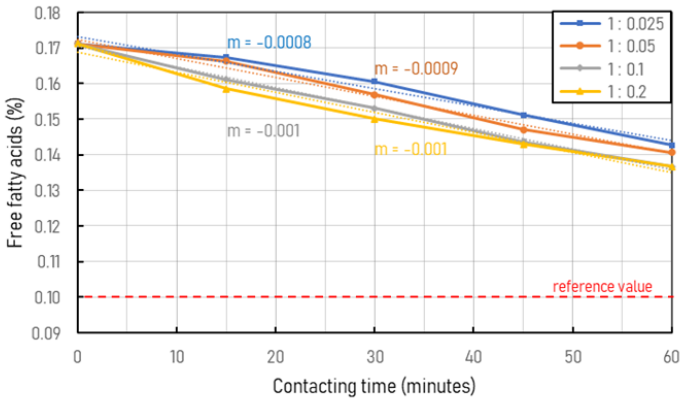

Fig. 3. fatty acid contents in purified UPO at several contact times and volume ratios

During the frying, the hydrolysis of PO will generate FFAs, and its production is dependent on temperature and heating time [28]. The American Oil Chemists' Society (AOCS) Official Method Ca 5a-40 recommends palmitic acid for determining FFA. The maximum value of FFA for the palm olein requirement is 0.1% (reference value), and it indicates the suitability for human consumption. Higher FFA values result in rancidity, causing offensive flavour.

Figure 4 shows the peroxide value plot against the contact time with 2.37 meq O2/kg for UPO for the non-contact time. At the longest contacting time, i.e., 60 minutes, peroxide values were 6.8%,

8.0%, 9.3%, and 9.3% for the volume ratios of 1: 0.025, 1: 0.05, 1: 0.1, and 1: 0.2, respectively. At higher volume ratios, the reducing peroxide values approached the reference value. The relative rate of reduction for all volume ratios was nearly the same, i.e., approximately 0.004 throughout the longest contact time. Thus, considering the cost of material and preparation for optimum use, the best parameter for the volume ratio to purify UPO was 1: 0.1.

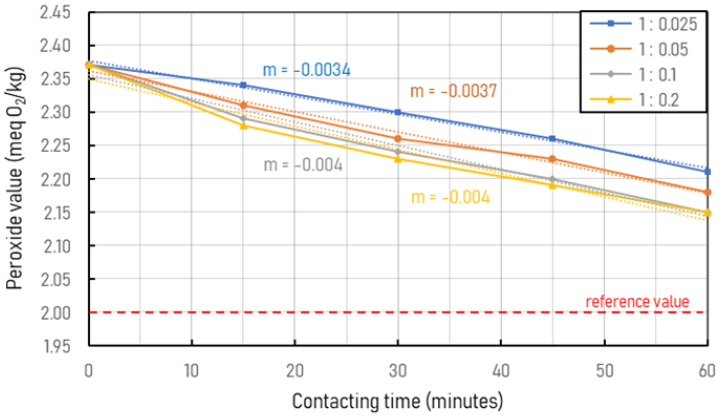

Fig. 4. Peroxide values of the purified UPO at various contact times and volume ratios

Peroxide value measures the oxygen content of peroxide, especially for oxidation products (e.g., oils and fats) and hydroperoxides [29]. It is estimated using the AOCS Official Method Cd 8b-90. The maximum peroxide value for the PO requirement is 0.2 meq O2/kg (reference value). This reference value also indicates the oil deterioration. High peroxide values result in a musty smell and rancidity as the oil is damaged by free radicals.

5. Conclusions

This study showed that DPAC adsorbed impurities by changing the colour/turbidity of UPO on a scale of 13 to 7. Also, the purified UPO improved in physicochemical characteristics with a 20.1% reduction in the FFA content, i.e., from 0.1712% to 0.1368 %, and a 9.3% reduction in the peroxide value (from 2.37 to 2.15 meq O2/kg 9.3%) for the volume ratios of 1: 0.1 and 1: 0.2. The improvements transformed the UPO to approach the reference values of virgin PO, i.e., 0.1% for FFA and 2.0 meq O2/kg for the peroxide value. In this study, the best parameter for the volume ratio (in unit gram) of UPO to the DPAC was 1: 0.1 with a contact time of 60 minutes at room temperature by taking into account the cost of material and preparation for optimum use.

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