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The efficacy and lipid degradation properties resulting from corncob biochar treatment for acrylamide reduction in reused palm oil

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ABSTRACT

Acrylamide is a carcinogenic compound commonly found in deep fried food. Given the health adverse effects of acrylamide, innovative techniques that can reduce acrylamide formation during frying is desirable while maintaining oil quality. This study examined how used palm oil treated with corncob biochar changed the amount of acrylamide and the composition of lipids. The biochar was mixed with used oil (ratio 1:10 (w/w)) for 15 h and the chemical properties of the oil were determined. The properties of biochar treated oil were compared with fresh oil, which formed the control, and used oil prior to biochar treatment. The results of oxidation (PV, TBARs) were significantly lower when the used oil was treated before being fried again. The use of biochar did not alter the fatty acid profile of the oil. Acrylamide content in fried potatoes was reduced by half compared to 2nd used oil (2 mg/100g) and 2nd used oil treated with biochar (0.8 mg/100g). This preliminary study shows that biochar made from agricultural waste has the potential to be used as an oil recycling material for a more sustainable alternative approach. Moreover, the method is applicable to industrial contexts and the material is safe for the environment.

1. Introduction

Palm oil is the cheapest vegetable oil to produce, partly because it has yields that are 6–10 times higher than those of other oil crops such as soy, rapeseed, sunflower, coconut and olive. In 2021, global production of palm oil totaled 72.9 million tonnes, while worldwide consumption came to the slightly higher total of 73.5 million tonnes, which represents 36.3% and 36.5% respectively of total global vegetable oil production and consumption.

Deep-frying or high-temperature frying is one of the most common procedures for the preparation of food by households and by food manufacturers. The 2017 survey of food purchasing behaviour in Thailand found that the majority of consumers bought fried foods, while minor groups of consumers bought roasted, steamed and boiled food (National Statistical Office of Thailand., 2017; Komin & Shabsing, 2011). Since there is high demand for fried food, the amount of palm oil used worldwide has increased from 66 million tonnes in 2017 to 73.5

million tonnes in 2020. In Thailand, the domestic consumption of refined oil has been increased from 1.16 million tonnes in 2017 to 1.23 million tonnes in 2021 (Chaiwat., 2022). This indicates an increasing trend to consume fried food and the amount of oil used for food preparation. A survey of the use of reused cooking oil in Thailand shows that more than half of food vendors reprocessed their cooking oil or kept the used oil for more cooking and repeated frying with the used oil 1–15 times (Komin and Shabsing., 2011). The consumption of reused oil can be a health concern, insofar as the oil used should be as clean and healthy as possible.

During frying there are several biochemical changes occurring in the oil, including degradation by oxidation, polymerization, hydrolysis, isomerization and Maillard reaction (Sikorski and Kolakowska., 2010). Consequently, the reuse of oil can potentially impact the physical quality, nutrition, and toxicology of products. Further, the product can also develop a caramelized flavour and crispy texture, in addition to containing oxidized lipids and acrylamide, which has been classified as a

Abbreviations: Frozen potatoes, FF; Chicken fillets, CK; Fresh oil, FO; 1st used oil, FC; 1st used oil treated with biochar, FCC; 2nd used oil, SC; 2nd used oil treated with biochar, SCC; total polar compound, TPC; peroxide value, PV; acid value, AV; thiobarbituric acid reactive substances, TBAR; fatty acid profile, FFA.

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group 2A carcinogen causing adverse health effects such as neurotoxicity and mutagenesis. (Dybing and Sanner., 2003). Hence it is important to seek a simple solution that can reduce acrylamide and polar compounds and that can be applied to street vendors and food sellers.

Waste cooking oil (WCO) collection from restaurants is approximately 11 billion liters annually. The application of WCOs are various, such as for use as yellow grease as a fuel source in bio diesel production, an ingredient in animal foods, and in soap production. Even though efforts succeed in collecting 15 million tons of WCO annually, only a little of the waste cooking oil is properly recycled. Monitoring and systematic management of WCO creates challenges to be faced, such as dumping the waste and causing water pollution.

Bioactive biochar is a high-carbon, fine-grained residue that is currently produced by pyrolysis from natural wastes such as corn cob and nutshell. Biochar is used for impurity absorption such as for the herbicide 2,4-dichlorophenoxyacetic acid, phenol and derivatives, Cu (II), Zn(II), Cd(II) and Pb(II) (Kolodyńska et al., 2012). Bioactive biochar has proven effective in the adsorption of heavy metals and for the removal of organic contaminants from aqueous media (Karakoyun et al., 2011; Kearns et al., 2014). However, there is no such innovative technique in the market that aims to reduce acrylamide formation in used oil. Consequently, using bioactive biochar as a tool for the reduction of undesirable products from deep-frying oil would extend its employ as a reused oil and reduce acrylamide content in final food products.

Through innovation, food processing efficiency and food safety can be improved, and food businesses can discover competitive advantages and economic opportunities for growth. The technology developed should also be readily implemented by food industry to create good social and environmental impacts.

Thailand is well-recognized as being among the top exporters of agricultural and food products and by-products of agricultural industries derived from post-harvest commodities such as bagasse, coconut shell and corncob. The estimated maximum production of corncob is 1.8 million tons per year (Wannapeera et al., 2008). Yet, the utilization of corncob is mostly limited to compost or cattle feed.

Valorisation has become a top priority in recent years because it is an increasing concern of the food manufacturing industry to reduce food waste and improve waste management (Mirabella et al., 2014). Strategies include supporting the development of a circular economy in the food sector by closing the loop and using wastes as resources, an approach being encouraged by recent policies in Europe (European Commissions, 2015; MacArthur E Foundation., 2015). Hence the research focus of this paper emphasizes both planetary health as well as human health.

The aim of this research is to examine the innovative use of biochar made from corncob for acrylamide reduction in deep fried palm oil. The research also aims at improving both nutrition and economic aspects to create healthier food and to reduce oil waste through the reuse of oil on both the industrial scale and the household level.

2. Materials and methods

2.1. Biochar production

Bioactive biochar was produced by pyrolysis of corncob in a local kiln at temperatures above 400 °C (Patent pending Number 2103003691). The kiln is prepared by lighting a fire, and then tossing pieces of corncob into it once the temperature reaches 400 °C. Corncobs were added until the kiln was full, so as to limit the level of oxygen. The corncobs began to turn black after about 6 h. The lid of the kiln was then closed and the contents allowed to smolder for at least 24 h. The resulting biochar was removed and cooled to room temperature prior to use.

2.2. Determination of morphology and chemical composition of biochar

2.2.1. Percentage of oil uptake in biochar

The percentage of oil uptake in biochar was measured from the weight of biochar before and after soaking in the oil. The calculation was performed using Eq. 1

$$\text{Percentage of oil uptake} = 100 - \left[\frac{\text{Weight of charcoal after soaking}}{\text{Weight of charcoal before soaking}} \times 100 \right] \quad (1)$$

2.2.2. Characterization of biochar

2.2.2.1. Morphological surface analysis by scanning electron microscopy (SEM). The morphology of biochar was measured following the method of Wongrod et al. (Wongrod et al., 2020). In brief, biochars were observed by SEM (JEOL JSM-IT500LA). SEM examination was performed at a magnification of 1200X and at an accelerating voltage of 10.0 kV.

2.2.2.2. Chemical composition of biochar. The analysis of biochar included fixed carbon, moisture content, ash, and volatile matter determination. Analytical methods were based on the standard method of the American Society for Testing and Materials Standards (ASTM 3172–3175) (ASTM, 1987).

2.3. Preparation of food samples for frying

Potatoes and chicken fillets samples were selected to represent carbohydrate and protein rich foods as these 2 types are common in fried food. Frozen potatoes (FF) were obtained as French fries (Carebout potatoes NV, Heirweh 26 B-8950 Nieuwerkerke, Belgium) and cut into rectangular pieces (1 × 1x6 cm). Chicken fillets (CK) were obtained from TESCO LOTUS (Ek-Chai Distribution System Co., Ltd., Nakhon Pathom, Thailand) and cut to the same size as the fries after removing the skin and washing with water. A domestic deep-fat fryer 1.2 L (OXYGEN, China) containing palm olein as the frying medium was used.

2.4. Deep-fat frying process

Samples of potato fries or chicken fillets weighing 250 g, were fried for 9 or 10 min respectively in 1 L of palm olein oil at 180 °C (USDA, 2013) which resulted in products that were deemed to be fully cooked and possess a golden brown color with the core temperature reaching 70 °C. After frying, the oil was drained from the product, and it was cooled to room temperature. The product was ground, weighed, collected, and stored at –20 °C until analysis.

2.5. Biochar treatment

Biochar was submerged in used oil (FC oil) in a 1:10 (w/w) ratio and left at room temperature for 15 h. The biochar was then removed, the oil was filtered through a multi-layer cloth, and the oil was reused in the second cycle of the frying process's (Fig. 1).

2.6. Determination of acrylamide content

Acrylamide content was determined by HPLC based on the method of Khoshnam et al. (Khoshnam et al., 2010) with some modifications. For acrylamide extraction, deep-fried food was defatted by using hexane and automatically shaken for 30 min. Then, defatted food samples were placed into 50 mL tubes and 20.0 mL acetone and 100 µl DI water were added. The sample tubes were placed in an ultrasonic water bath (Branson® CPX1800H, USA) at 40 °C for 20 min and the aliquots collected, filtered, and dried at room temperature. After the acetone was completely evaporated, 2.0 mL of HPLC grade water were added and

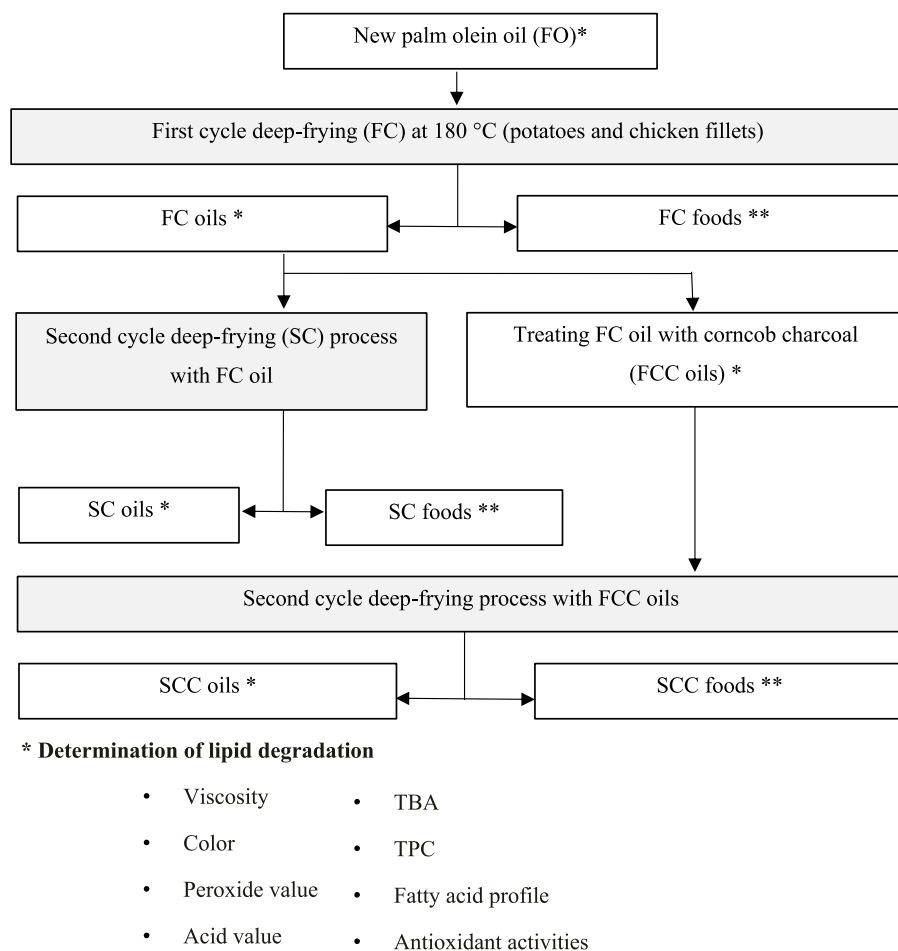


Fig. 1. Conceptual framework of the research.

shaken well. The solution was filtered through a filter paper before being injected into the HPLC system (Agilent 1200 series, USA). An acrylamide standard stock made from 1 mg/mL (Merck, Germany) was prepared in water. Aliquots of acrylamide stock were diluted for construction of the calibration curve. A C18 column (Phenomenex, USA, 250 mm × 4.6 mm i.d. 5) was employed in the HPLC using acetonitrile and water (20:80) as the mobile phase (adjusted pH 3.5 with orthophosphoric acid). Injection volume was 20 µL with a flow rate of 1.0 mL/min and the wavelength monitored by a UV detector was set at 225 nm.

2.7. Acrylamide adsorption testing

The acrylamide standard solutions were prepared at two concentrations (50 and 100 mg/kg) as it was higher than the average amount found in deep-fried potatoes in this study and other research (Chen et al., 2012; Chuang et al., 2006; Khoshnam et al., 2010). Biochar was submerged in the standard solution individually, using the same condition with the used oil (FC oil). Acrylamide content was determined by HPLC as describe previously. The percentage of acrylamide reduction in solution was evaluated by using Eq. 2

$$\text{Percentage of acrylamide reduction} = 100 - \left[\frac{\text{Acrylamide content after soaking}}{\text{Initial acrylamide content}} \times 100 \right] \quad (2)$$

2.8. Determination of lipid properties

2.8.1. Determination of viscosity and color

Oil viscosity was determined using a concentric cylinder viscometer (model LVT, Brookfield, Stoughton, MA) at 25 ± 2 °C (Udomsinka et al., 2019).

2.8.2. Determination of acid value (AV) and peroxide value (PV)

The AV and PV was determined by titration based on the method specified by American Oil Chemists' Society, AOCS (AOCS, 1997; AOCS, 1998). The data was expressed as mg KOH/g oil for acid value and meq/kg oil for peroxide value.

2.8.3. Determination of thiobarbituric acid reactive substances (TBARs)

TBARs of oil was determined by measuring the absorbance of sample solution at 532 nm using a spectrophotometer (TECAN Group Ltd., Switzerland); malondialdehyde solution was used as a standard. The TBARs was expressed as µmol per gram of oil. (Zeb and Ullah., 2016).

2.8.4. Determination of total polar compounds (TPC)

The TPC was determined by a Food Oil Monitor FOM 330 (Ebro, Germany) as a rapid measurement (Chen et al., 2013). The oil sample was heated to 120 °C and the probe of the monitor immersed for 10 min, prior to recording the reading. The result was expressed as percentage of TPC.

2.8.5. Determination of fatty acid profile (FFA) of oil samples

The fatty acid profile was determined by GC-FID based on the method of Jham et al. (Jham et al., 1982). The methylation was used boron trifluoride-methanol reagent. The fatty acid methyl esters was analyzed with GC System (Agilent 6890N, USA), equipped with a RTTM-2560 column with dimensions of 100 m × 250 μm and 0.2 μm inside diameter (Restek Corp., USA) and flame ionization detector. The column oven was preheated for 10 min at 60 °C–160 °C, then elevated to 200 °C for 40 min and retained at 220 °C for 18 min. The carrier gas was helium, with a flow rate of 2 mL/min and a split inlet of 1:100. The reference standard was used to identify the fatty acid methyl esters.

2.8.6. Oxygen radical absorbance capacity (ORAC) and ferric reducing antioxidant power (FRAP)

ORAC and FRAP were performed according to Somsong et al. (Somsong et al., 2020). The results were expressed as μmol trolox equivalent per 100 g of oil.

2.9. Experimental design and statistical analysis

A Randomized Complete Block Design (RCBD) was used. The results are presented in the form mean ± standard deviation (SD). The difference between samples was examined based on ANOVA with the Duncan's multiple range test and the significance level set to a percentage of 5 ($P < 0.05$) to evaluate the differences between the tested values. The statistical analysis was performed by SPSS Statistical Software version 18.0.

3. Results and discussion

3.1. Efficacy of biochar, acrylamide absorption and oil uptake

3.1.1. Acrylamide adsorption testing

To determine the ability of biochar to absorb acrylamide, the acrylamide standard solution was prepared at high concentrations (50 and 100 mg/kg) since it was higher than the average amount found in deep-fried potatoes in this study and other research (Chen et al., 2012). This observation was an indirect way to examine whether the use of biochar could cause reduction of acrylamide at higher concentration. The data is reported in Fig. 2A. The results show that acrylamide solution not treated with biochar exhibits a tiny percentage of acrylamide around 1%, which may be due to loss when stored at room temperature. Previous research indicates that acrylamide loss occurs after storage at 25 °C through some mechanism such as, polymerization under UV light

and evaporation (Michalak et al., 2016). Acrylamide content in the solution treated biochar was lower compared to the initial solution by 24.82 ± 1.38 to $27.13 \pm 0.20\%$. In any case, this study carried out the reduction of acrylamide in aqueous solution by using biochar as an absorber, for which real samples are needed for better understanding.

3.1.2. Percentage of oil uptake in biochar and absorption mechanism

The absorption capacity in biochar depends on several factors, such as the type of biochar, the original biomass composition, hole particle size, amount and shape of porosity, surface area, and pyrolysis temperature (Josept et al., 2020). Corncob biochar had $38.84 \pm 2.21\%$ of weight uptake after soaked in oil. The liquid holding capacity of different biochars was not equal since it depends on their physical and chemical characteristics (Gondim et al., 2018).

The absorption capacity properties of biochar play a major role in acrylamide removal. Several mechanisms such as physical absorption due to its porosity, surface precipitation due to its structure, functional group complexation, cation and anion attraction due to its surface functional groups and also ion exchange can be simultaneously occurring (Huang et al., 2019; Josept et al., 2020). Most biochars were highly porous and had a large surface area for absorbing soluble substances, as shown in Fig. 3. The direct impact is due to its enormous interior surface area and high number of residual holes, which hold oil by capillary action (Batista et al., 2018). The chemical composition of biochar was linked to its properties, as given in Table 1. The biochar is rich in carbon and contains fixed carbon. Raising the pyrolysis temperature over 400 °C during biochar production described in this paper, improves biochar carbonization and leads to higher fixed carbon content and increased electrostatic interaction with chemicals, allowing it to adsorb more acrylamide. Thus, the biochar with more fixed carbon biochar shows the potential to interact with more acrylamide when soaked in the liquid phase. In addition, the rise of biochar production temperature has a positive impact on higher pore surface area and increased absorption (Batista et al., 2018).

Moreover, sorption of complex compounds can be possible owing to the presence of functional groups in biochar, by the exchange/attachment of various associated anions like oxide/peroxide ion (O_2^{2-}) and cations like H^+ (established in acid, acrylamide, and some carbonyl compound ends) on biochar surfaces. This is supported by research performed by Ambaye et al. (2020), who found that functional groups that included oxygen in their structure, including phenolic, lactonic, and carboxyl, would allow biochar to bond with other compounds. The presence of oxygen can accelerate biochar surface oxidation, resulting in increased cation-molecule complexation. Accordingly, some acrylamide precursor may be absorbed by biochar's structural ions, as well as by oxidized compounds in used oil.

Additionally, the lignocellulosic composition was different in each material. The study of Ukanwa et al., 2019 presented an analysis of the lignocellulose contents of biochar materials as determined by biochemical analysis (Ukanwa et al., 2019). Corn cob components had high carbon, oxygen and contained lignin as natural fiber (18.27%). Lignin is an insoluble natural polymer with aldehydic and carbonyl groups, making it strongly polarized (Ukanwa et al., 2019). It was established that lignin is a widely accessible and well-studied antioxidant that encompasses a large number of phenolic compounds, enabling it to act as an effectual antioxidant to remove potentially damaging oxidizing agents. This is one possible way to reduce oxidative reactions by reducing radical scavenging activity in lipid oxidation through carbonyl trapping effects, and limit sugar degradation in Maillard reaction (Mahmood et al., 2018, pp. 181–205; Zhang and Jin., 2015). Moreover, lignin shows the ability to adhere to acrylamide to form lignin acrylamide complexes (Wang et al., 2016). Thus, the materials that contain lignin show an ability to mimic those unfavorable substances in used oil.

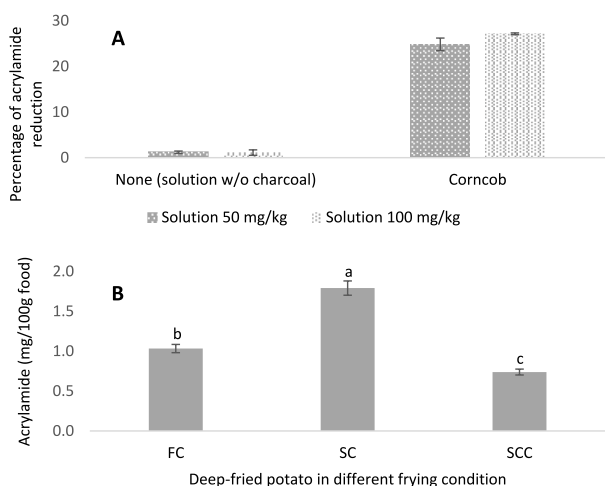


Fig. 2. Percentage of acrylamide reduction when soaked in acrylamide solution (A) and acrylamide content in fried potato in different frying conditions (B).

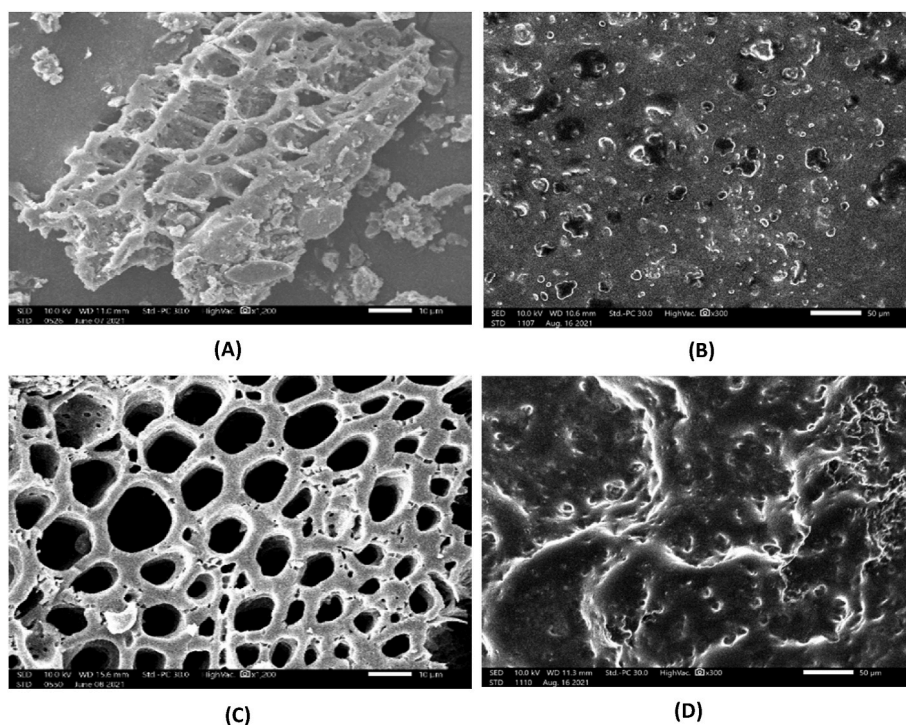


Fig. 3. Morphological surface of corncob charcoal, before soaked in oil (A), after soaked in oil (B), cross-sectioned before soaked in oil (C), and cross-sectional after soaked in oil (D). Scale bar = 10 μm for images A and C and 50 μm for images B and D.

Table 1

Chemical composition of corncob charcoal (g/100 g).

Chemical Composition	Content (g/100 g)
Fixed carbon	65.55
Moisture content	5.00
Ash	10.25
Volatile matter	19.30

3.1.3. Acrylamide reduction

After cooking at high temperatures, acrylamide can occur spontaneously via chemical reactions in some types of starchy foods (Chen et al., 2012). The amount of acrylamide in deep-fried potatoes in our study is reported in Fig. 2B. The quantitative analysis of acrylamide revealed that deep-fried potatoes from SC contained the most acrylamide when compared to FC and SCC. Acrylamide content in fried potatoes increased through repeated frying processes as reported by Mekawi et al. (Mekawi et al., 2019). Fried potatoes from the oil treated with corncob biochar (SCC) showed a significantly lower acrylamide content than untreated batches (SC). However, the acrylamide could not be detected in deep-fried chicken. This is attributable to the limit of detection in this analysis method (3.7939 $\mu\text{g/g}$). Some studies agree that acrylamide was found primarily in carbohydrate-rich foods and was not found in chicken muscle other than in the external starch layer which was not used in this study (Chuang et al., 2006).

3.2. Characterization of corncob biochar

The biochar produced at 400 $^{\circ}\text{C}$ in a traditional local kiln. The size of each biochar pallet was approximately 70 \times 30 \times 20 cm. The surface morphology of biochar determined by SEM as shown in Fig. 3. The surface is structurally complex and comprises many pores having diameters in the range 2–10 μm . Biochar has an exceedingly intricate network of pores and channels, as well as a fibrous surface. An analysis of biochar is given in Table 1. The chemical composition of corncob charcoal is fixed carbon (65.55 g/100 g), moisture (5 g/100 g), ash

(10.25 g/100 g), and volatile matter (19.31 g/100 g). The biochar efficacy was influenced by a variety of parameters such as the use of corncob, its particle size, porosity, surface area, and pyrolysis temperature (Josept, et al., 2020). The pyrolysis temperature in the local kiln was not controlled precisely as is possible in a modern kiln. However, the temperature was over 400 $^{\circ}\text{C}$ for a considerable period of time, which is high enough to pyrolyze the corncob into biochar (Tiyayon et al., 2016). It may be noted that the adsorption capacity of biochar also depends on factors such as percentage of fixed carbon which helps retain polar compounds. (Ambaye et al., 2020).

3.3. Deep-fried food and deep-fried oil appearance after treated with biochar

Fried food appearance is shown in Fig. S1 (supplementary data). There were no differences in the appearance of fried chips between the 1st and 2nd cycle of deep frying. The oil samples from 1st and 2nd frying cycles showed some difference in color (Fig. S2, supplementary data). The used oil was darker than fresh oil. In addition, the oil treated with biochar (SC) did not change in appearance. This indicated that biochar treatment does not influence the oil appearance.

3.3.1. Color

L^* , a^* , and b^* of deep-fried oils are presented in Fig. S3A (supplementary data). L^* values of oils after frying (FC and SC) are significantly lower for all treatments. The values of a^* after frying are only marginally different in comparison with fresh oil. The redness value (a) was reduced marginally after frying, with a significant difference in SC oil. For b^* , FC and SC oils were slightly different in their yellow color and both were more yellowish than FO oil. It was discovered that extending the frying time resulted in a modest reduction in lightness and greenness of the oil, but faintly increased in their yellowness (Sunisa et al., 2011). When comparing the oil with and without biochar treatment (FC and SC to FCC and SCC), there were no statistically significant differences in terms of lightness, redness, and yellowness. Corncob biochar in fried oil has no effect on the color of the oil.

3.3.2. Viscosity

Viscosity is a crucial factor for oil in relation to the application and the oil quality. The analysis of our data is presented in Fig. S3B (supplementary data). The viscosity of used oil (FC and SC) was significant higher than compared to FO. SC oils had the highest viscosity in these cases, which agreed with many studies indicated that with longer frying time there is a marginal increase in viscosity in used-fried oil (Sunisa et al., 2011). The higher viscosity in frying oils is due to oxidation and polymerization, as well as the production of high molecular weight polymers that form during high temperature frying (Sunisa et al., 2011). When the oils with and without biochar treatment are compared, there were no statistically significant differences in viscosity. Hence, using corncob biochar in fried oil will not have a significant effect on oil viscosity.

3.4. Lipid degradation parameters in deep-fried oil

3.4.1. Peroxide value

The deep-frying procedure can impact not only physical but also chemical properties of oil. The process creates both favorable and unfavorable chemical change, as well as affects the taste consistency and quality of the oil by hydrolysis, oxidation, and polymerization as the main reactions in the process. In all biochar treatments, SC oil peroxide values were significantly higher than the FO and FC (Fig. 4A). These findings agree with those of many researchers (Goswami et al., 2015; Jurid et al., 2020). It was found that peroxide values are raised by repeated frying, indicating the oxidation reaction is gradual.

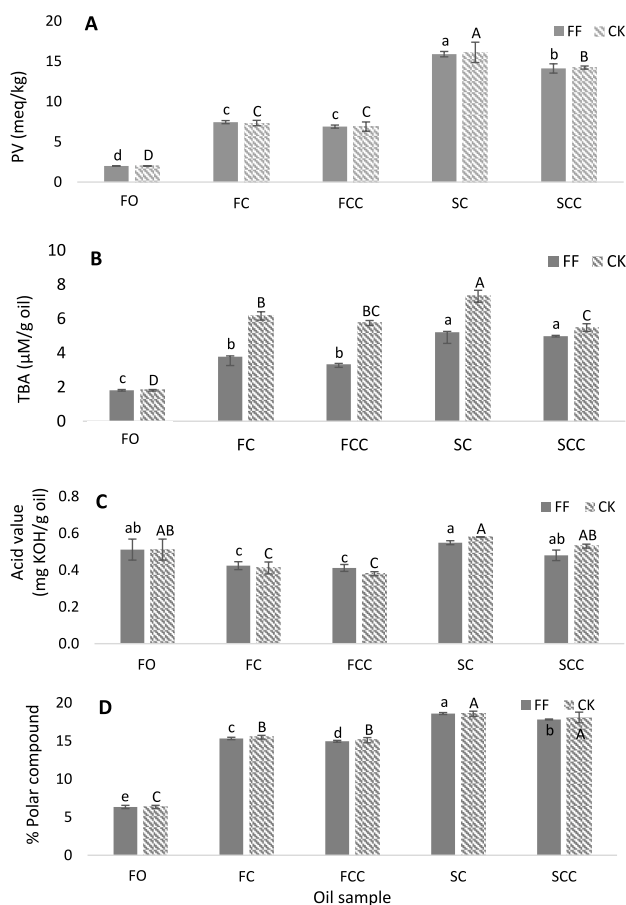


Fig. 4. PV (A), TBAR (B), Acid value (C), and %TPC (D) of deep-fried oil in the different treatment (FO, FC, FCC, SC, and SCC) (Small letters shown the significant difference between oil from deep-fried potatoes. Capital letters shown the difference between oil from deep-fried chickens, $P < 0.05$).

Remarkably, the used oil that is treated with biochar comprises a significantly smaller amount of peroxide compared to untreated oil in SC. But when comparing FC oil peroxide values between treated and untreated biochars, FCC had a slightly lower amount of peroxide. Yet, in this study, peroxide values in FC oils were not in excess of food act regulation, which is 10 meq/kg (FDA., 2000).

3.4.2. Thiobarbituric acid reactive substances (TBAR)

FC and SC oil were significantly higher in TBAR than FO. This observation is consistent with prior research demonstrating that TBAR was related to the converting of peroxides to carbonyl and aldehyde molecules identical to MDA, which can be triggered by the heating process (Falade and Oboh., 2015). SC oil showed the highest value for both potatoes and chicken, followed by SCC oil (Fig. 4B). This indicates that frying protein resulted in higher TBAR and that the use of biochar immersion can reduce TBAR to similar levels as FC. Regarding the effect of biochar application in FC and FCC, there were no differences on TBARs.

3.4.3. Acid value (AV)

The acid value of fried-oil is shown in Fig. 4C. The oil without biochar treatment showed no significant difference when including FO, FC, and SC. However, the acid values in FC oil, both with and without biochar treatment, were slightly lower than those in SC and FO oils. These may be due to the loss of free fatty acids during FC, which is related to the balance of triglyceride hydrolysis and degradation reactions, or the volatilization of free fatty acids during the frying process, resulting in a reduction of free fatty acid (Li et al., 2016). The acid value in frying oil can be increased by increasing frying temperature and time through hydrolysis rancidity (Li et al., 2016). However, none of the acid values were more than 0.6 mg KOH/g oil, which is the limit set for most oil specifications (FDA., 2000).

3.4.4. Total polar compounds

During frying, a variety of volatile and non-volatile by-products are formed, including free fatty acids, alcohols, cyclic compounds, dimers, and polymers. The total polar compounds (TPC) category encompasses the bulk of non-volatile by-products in oil from deep-frying processes. TPC concentration is one of the most common measures of oil quality, and it is widely utilized in many international laws (Chen et al., 2012). The quantity of TPC in frying oil should not exceed 25 g/100 g oil due to public health implications (FDA, 2004). The percentage of total polar compounds are reported in Fig. 4D. The results show that TPC is significantly higher when increasing the frying cycle, as the values were the highest in SC oil. These results indicate that primary and secondary oxidation from the frying process is intimately linked to the formation of polar molecules, and implies oil degradation. Moreover, it is possible that frying conditions increase cyclization, polymerization, pyrolytic, hydrolytic, oxidative, and other chemical processes that generate non-volatile by-products (Chen et al., 2012; Choe and Min., 2007). Comparing the oils with and without biochar treatment, there was a significant decrease in TPC in SC oil, while FC oil treated with biochar showed a slight decrease in TPC. This could be due to the greater amount of TPC in SC oil. Nevertheless, the content of TPC in all oil samples was not greater than 25 g/100 g oil, which is the acceptable maximum value of reused oil (FDA, 2004).

3.5. Oil quality after biochar treatment

3.5.1. Fatty acid profile

Fatty acid profile was used to determine oil quality, since fatty acids experience chemical modifications that render fried oil nutritionally variable. The percentage of fatty acid composition of these deep-fried oils at 180 °C is shown in Table 2. Medium chain fatty acids (C12–C18) were found in all oil samples with a slight difference between treatments. There were lauric acid (C12:0), myristic acid (C14:0),

Table 2
Fatty acid composition (%) of deep-fried oil in the treatment of corncob charcoal.

Fatty acid	FO	Oil from deep-fried potatoes				Oil from deep-fried chickens			
		w/o charcoal		with corncob charcoal		w/o charcoal		with corncob charcoal	
		FC	SC	FCC	SCC	FC	SC	FCC	SCC
C12:0	0.32 ± 0.07	0.32 ± 0.00	0.30 ± 0.01	0.32 ± 0.01	0.31 ± 0.00	0.30 ± 0.00	0.28 ± 0.03	0.34 ± 0.02	0.30 ± 0.00
C14:0	0.95 ± 0.03 ^a	0.90 ± 0.00 ^{ab}	0.89 ± 0.00 ^{ab}	0.95 ± 0.00 ^a	0.84 ± 0.00 ^b	0.86 ± 0.05 ^c	0.88 ± 0.02 ^c	0.96 ± 0.04 ^B	1.21 ± 0.10 ^A
C16:0	37.75 ± 0.30 ^b	36.94 ± 0.07 ^b	37.43 ± 0.07 ^b	37.44 ± 0.07 ^b	38.25 ± 0.04 ^a	37.27 ± 0.04	37.36 ± 0.19	37.10 ± 0.48	37.63 ± 0.27
C18:0	2.98 ± 0.00	3.08 ± 0.03	3.05 ± 0.04	ND	ND	3.06 ± 0.04	3.14 ± 0.05	ND	ND
C18:1trans (n-9)	ND	ND	ND	3.4501 ± 0.03	3.4211 ± 0.01	ND	ND	3.70 ± 0.056	3.63 ± 0.27
C18:1cis (n-9)	ND	ND	ND	48.3299 ± 0.05 ^a	45.0919 ± 0.04 ^b	ND	ND	48.22 ± 0.15 ^A	46.41 ± 0.17 ^B
C18:2t9t12	48.41 ± 0.12	48.12 ± 0.10	48.42 ± 0.10	ND	ND	48.29 ± 0.07	48.22 ± 0.03	ND	ND
C18:2n6 (e9c12)	10.50 ± 0.07 ^b	10.32 ± 0.02 ^b	10.21 ± 0.07 ^b	9.91 ± 0.06 ^c	11.20 ± 0.02 ^a	10.25 ± 0.09 ^A	10.36 ± 0.09 ^A	9.68 ± 0.25 ^B	10.27 ± 0.23 ^A

b. Superscript small letters show the significant differences between oils from deep-fried potatoes. Superscript capital letters show the differences between oils from deep-fried chickens ($P < 0.05$).

d. ND = Not detected.

^a Values mean ± SD (n = 3).

^c . C4:0, C6:0, C8:0, C10:0, C18:b (n-9,12), C18:b (n-6), and C18:c (n-c) were not detected.

palmitic acid (C16:0), steric acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), and linoleic acid (C18:2), and linoleic acid (C18:2t9t12). The type of fatty acid found in palm oil was similar to those indicated by other research (Mancini et al., 2015). Other types of fatty acid that were not found in this study can be attributable to the limit of detection in the analytical method (0.04% fatty acid, 0.06 mg/100g), thus not in any major concentration in palm olein oil. For corncob biochar treatment, significant differences were demonstrated in SCC, and some changes in fatty acid, C18:1trans (n-9) and C18:1cis (n-9) were found in both FCC and SCC. Nonetheless, the effect of biochar on the change of fatty acids in oil was not found. As a result, disparity of the fatty acid profile in different conditions of frying oil could come from the severe cooking process as shown by Multari et al. (Multari et al., 2019), in which the degree of change occurred after 60 min of the heating process at 180 °C. The differences were relatively small, and short-term deep-frying suggested a good fatty acid profile stability.

3.5.2. Antioxidant activities

Antioxidant activities in oil is another oil quality with influences on oil stability and nutritional benefits of the oil. ORAC and FRAP were examined in the oil samples. The ORAC values reflect the peroxy radical scavenging activity. FRAP values reflect antioxidant capacity by the reduction of ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}) by antioxidants present in the samples (Ou et al., 2002). ORAC values of all samples are presented in Fig. 5A. FRAP values are presented in Fig. 5B. Based on these results, ORAC and FRAP values did not interrelate. The result show that most FO had greater ORAC and FRAP when compared to heated oil. But some of the heated oils in both FC and SC had a higher value. These were related to the effect of cooking method on the change of antioxidants. The initial stage of thermal processing could promote some of the oils' soluble antioxidant compounds, such as tocopherols, phenols, vitamin E, and natural antioxidants in palm oil, and improve the release of bound phenolic compounds in food matrices (Thanuja et al., 2019). In contrast, the lower value of antioxidant activities in heated oil could come from dejection through repeated heating and the destroying of antioxidant substances, notably vitamin E via increasing cooking temperature (Masbah et al., 2017). Comparing the oil with and without biochar treatment, the oil samples from every frying batch showed fluctuating antioxidant activities due to non-changed, reduced and increased ORAC and FRAP values. This was due to the indirect or direct effect of biochar on the change of antioxidant activity, which no research has previously discovered. In any case, the increase in antioxidant activity of oil after soaking biochar could be attributed to lignin, a

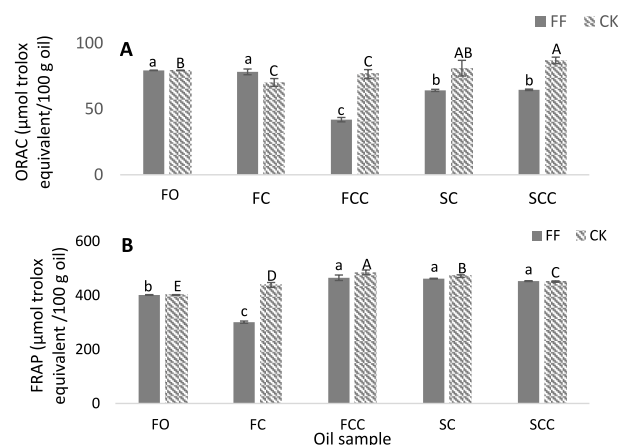


Fig. 5. Antioxidant activity, ORAC (A) and FRAP (B) of deep-fried oil in the different treatment (FO, FC, FCC, SC, and SCC) (Superscript small letters shown the significant difference between oil from deep-fried potatoes. Superscript capital letters shown the difference between oil from deep-fried chickens, $P < 0.05$).

natural antioxidant found in all types of biochar (Mahmood et al., 2018, pp. 181–205). Also, some derived coal has proved to contain antioxidants (Nilewski et al., 2019). In any case, the reduction of these values in biochar treated oils could come from some reduction activity such as surface complexation or ion attraction on the biochar surface that is able to trap charged ions in liquid phase (Josept et al., 2020). However, this issue remains a question and it should be further investigated.

4. Conclusions

The use of corncob demonstrated the potential to reduce PV, TBAR, TPC in reused palm oil. Acrylamide content in fried food was reduced up to 30% by the application of biochar. In addition, using biochar did not significantly affect the color, viscosity, free fatty acid, fatty acid profile, and antioxidant activities in reused oil. Consequently, the use of biochar in reused oil would expand on methods for lowering the negative health effects by reducing oxidized compounds in used oil and by a reduction in acrylamide formation and consequently the risk of cancer. The benefits of biochar use could be both nutritional and economical, since it could

produce healthier fried-food and minimize oil waste by repurposing it. In addition, the application of how to use biochar on used oil is simple and easy to apply. This purpose can be implemented on both the industrial scale and at the household level through slight adjustment. Nonetheless, this study demonstrates the potential of biochar on the change of lipid deterioration and acrylamide content. A study of biochar absorption mechanisms on unfavorable substances in oil is needed to further promote its employ in real practice.

CRedit authorship contribution statement

Wimphan Chathiran: Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Nattira On-nom:** Writing – review & editing, Writing – original draft, Supervision, Methodology. **Pimpinan Somsong:** Writing – original draft, Supervision, Resources, Methodology. **Pimsiri Tiyyayon:** Writing – original draft, Supervision, Methodology, Conceptualization. **Keshavan Nir-anjan:** Writing – review & editing, Writing – original draft, Validation, Resources, Methodology, Conceptualization. **Warangkana Sricham-nong:** Writing – review & editing, Writing – original draft, Validation, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.lwt.2023.115720>.

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