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Recovery of used frying palm oil by acidified ash from rice husk

Sakulthaijaidee Nattaporn, Thamakorn Porjai*

Faculty of Agro-industry, King Mongkut's Institue of Technology Ladkrabang, 10520 Ladkrabang, Bangkok, Thailand.

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ABSTRACT

The objective of this study is to improve the quality of fried palm oil by rice husk ash (RHA) adsorption. The RHA was prepared with and without acid treatment. For acid treatment, rice husk was soaked in two different acids, one was 10 M HNO_3 for 24h, and other was 3M HCl for 3 h. Rice husk (200g) was suspended in 500 ml of acid, thereafter, it was washed with distilled water to obtain pH 7 before incineration at 550°C for 12h. For untreated-RHA, rice husk was incinerated at the same temperature without acid treatment. The RHA (20 g) was mixed with 100 g used oil and stirred at 500 rpm on electrical heater at 80°C for 30 min to perform adsorption process. The RHA was filtered out and filtrate oil was analyzed for total polar compound (TPC), free fatty acid (FFA), peroxide value (PV), color *L* a* b**, and viscosity. Results showed that the acids-treated RHA with HCl and HNO_3 could significantly *(p<0.05)* reduce TPC of the original used oil from 10.17% to 4.39% and 4.17% respectively, whilst untreated-RHA could significantly *(p<0.05)* reduce TPC to 7.87%. The acids-treated RHA significantly *(p<0.05)* increased *L** (brightness) value of used oil from 41.30 to 88.93 (HCl) and 88.85 (HNO_3), whereas to 83.21 for the untreated-RHA. However, the PV and FFA improvement of used oil after adsorption process using untreated-RHA was significant *(p<0.05)* higher than those of both acids-treated RHA. The both acids treatments of RHA had no significant difference *(p>0.05)* for all determining quality parameters of the used oil.

* *Corresponding author*: Tel.: +66-897-710-258; fax: +66-2329-8526
Email: kthamako@kmitl.ac.th

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INTRODUCTION

Edible oil plays a very important role in cooking and food productions. Deep fat frying with high temperature from 150 to 190°C is the oldest and popular food preparation to make desirable flavor, color and crispy. During deep frying, triacylglycerol in oil are decomposed to di/mono-acyglycerol, glycerol, free fatty acid, polar compounds and other decomposition materials caused from the heated oil contact with water, oxygen and food ingredients (Choe and Min 2007; Chung *et al*., 2004). Those free fatty acid (FFA), total polar compounds (TPC) and peroxide value (PV) indicate the degree of decomposition in oil. Color and viscosity also indicate the physical properties of oil to consumers. In Europe, the regulatory limits of TPC range to 24-25 % (Wai*et al*., 2007). Rice husk is a by-product generated from rice mill, corresponded about 22% of the initial weight of paddy. Its ash produced up to 95% of silica powder after incineration at high temperature (Della *et al*., 2002). Many researchers found that leaching rice husk using solution of HCl, HNO_3, H_2SO_4, NaOH and NH_4OH and boiling before high temperature treatment from 500 to 1400°C could remove metallic impurities and produce white ash-silica with high specific surface area (Chakraverty*et al*., 1988; Mishra *et al*., 1985; Patel *et al*., 1987). Farook and Ravendran (2000) reported that rice hush ash produced by acid treatment (14M HNO_3 for 24 h) before thermal treatment could increase specific surface area and adsorptive capacity to remove FFA in used oil. Therefore the objective of this research is to study the adsorption ability of two different acids (HCl and HNO_3) treated rice husk ash (RHA) to improve the qualities of fried palm oil through the measuring improvement in quality parameters of FFA, PV, TPC, color, and viscosity.

MATERIALS AND METHODS

Used frying oil sample

The used frying oils were collected from a deep-fried chicken shop in Samutprakarn market, Thailand. Those palm oils were used to fry chicken at about 170°C for 4 hours per day and continuously used until 7 days. The coating ingredients of the fried chicken included wheat flour, rice flour, garlic, sugar, pepper and salt. The oils were determined for their quality including peroxide value (PV), free fatty acid (FFA), total polar compound (TPC), color and viscosity.

Rice husk ash preparation

Rice husks were obtained from a local rice mill (Samutprakarn, Thailand).These husks were washed with water to remove adhering dirt particle and dried overnight at 110°C. Thereafter, rice husks were ground by hammer mill and then pin mill with sieve size of 250μm. For acid treated-RHA, rice husks (200 g) were soaked in 500 ml of two different acids, one was 10M HNO_3 for 24h, and other was 3M HCl, for 3h,after which they were washed with distilled water until pH 7 and dried overnight at 110°C before incineration in muffle furnace at 550°C for 12h. For untreated-RHA, rice husks were suddenly burned at the same temperature without acid treatment. The rice husk ashes were kept in dry place until use.

Adsorption method

Used oil sample (100 g) was heated until 80°C by electric heater, 20g of RHA was mixed to the heated oil and continuously stirred at 500 rpm for 30 min at this controlled temperature. The filtration was done using vacuum pump and Whatman No.1 filter paper to remove the RHA. The filtrate oil was analyzed for the quality parameters.

Quality parameters

FFA and PV was determined by AOCS Official Method Ca 5a-40 and Ca 8-53 (AOCS, 1998), respectively. TPC was measured by FOM 310 (Ebro Electronic GmbH) and viscosity was measured at 25°C using Brookfield viscometer (Brookfield DV III).Color L^*, a^*, b^* was measured using Hunter Lab (Color Quest XE).

Data analysis

All data analysis were conducted in triplicate and expressed as means ± standard deviations (SD). The results were analyzed by the computer statistic program and 0.05 statistical level was considered as significance.

RESULTS AND DISCUSSION

The amount of oil yields from adsorption process was about 60% and they were not significantly different (p>0.05) among the untreated and the two acidified RHA samples (Data not shown).

The PV in original used oil was 6.88 meq/kg. After treating with RHA, the values were reduced, as shown in Figure1 and Table1, the untreated-RHA (3.74 meq/kg, reduced45.32%) showed significant (p<0.05) lower PV value than the HCl-treated (5.41 meq/kg; reduced 19.29 %) and HNO_3-treated (5.92 meq./ kg, reduced 20 %) RHA. It was observed by Wannahari and Nordin (2012) when using 7.5 g of bagasse for 10 min contact time could reduce PV in used palm oil about 21%. The FFA content was reduced from the original used oil (0.97%) by either using untreated or acid treated RHA. However, the untreated RHA (0.35%, 56% reduction) showed higher reduction of FFA than HCl-treated (0.45%, 44% reduction) and HNO_3-treatedRHA (0.46%, 49% reduction) (Figure1 and Table1). Song *et al*. (1998) found a commercial adsorbent like hubersorb (600) in which contains mostly with calcium silicate had ability to remove FFA by 84.5%. It is noticeable that the untreated-RHA could reduce PV and FFA of used oil better than the acid treated ash, which might be due to the simultaneously occurring of oxidation and hydrolyzation reaction during heating of the oil with catalyzing from the minimal acid residue in acids-treated RHA.

Table 1 Relative reduction (%) on quality parameters of used oil after adsorption process

Parameters	Relative reduction		
	Untreated-RHA	HCl-treated RHA	HNO_3-treated RHA
Peroxide value	45.32±2.86[b]	19.29±2.89[a]	20.00±2.90[a]
Free fatty acid	56.51±2.16[b]	44.00±2.16[a]	46.90±2.18[a]
Total polar compounds	23.60±4.70[a]	57.97±4.70[b]	59.56±4.70[b]
Viscosity	2.58±1.03[a]	5.13±1.02[ab]	6.93±1.02[b]

Values express in mean (±SD); the same small letters in the same row are not significantly (p>0.05) different.

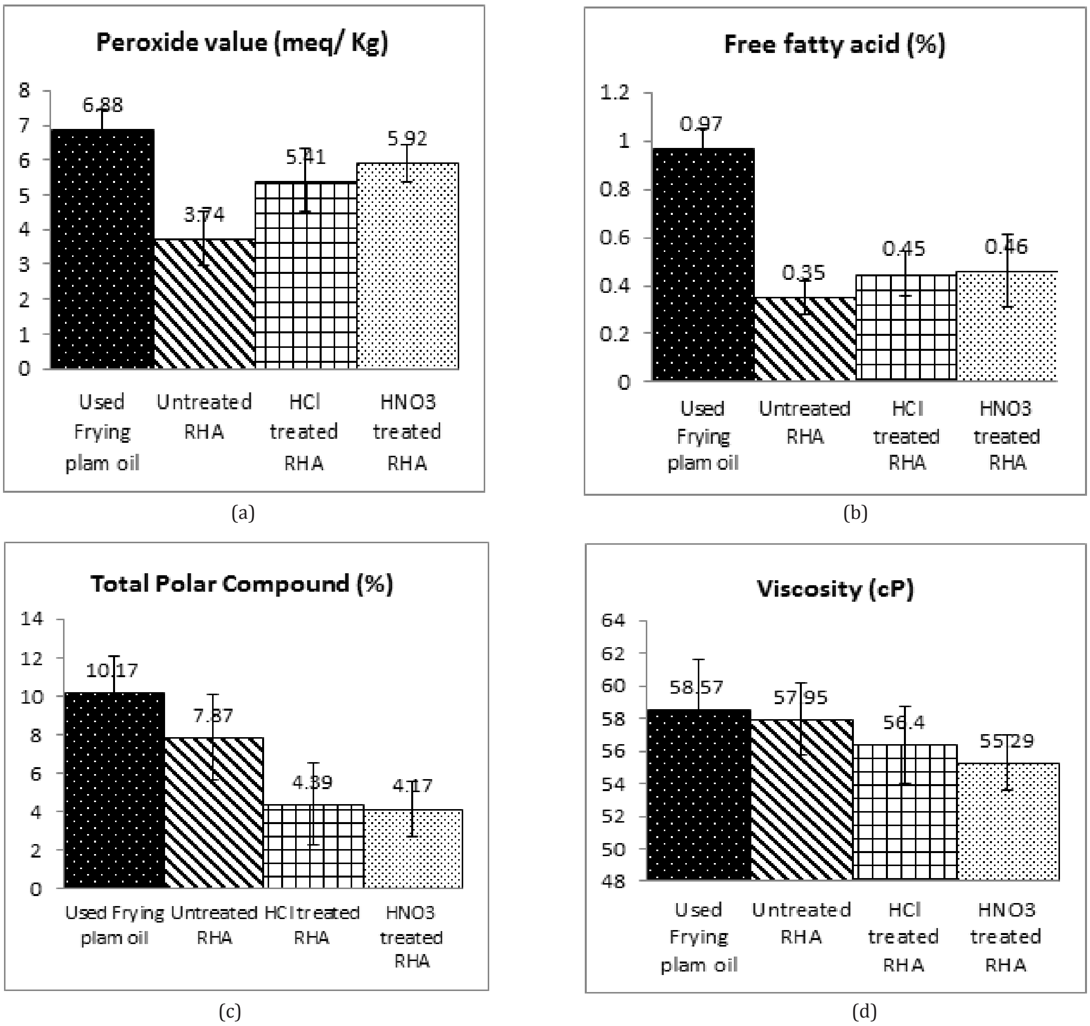

Figure 1 Peroxide value (a), Free fatty acid (b), Total polar compounds (c) and Viscosity (d) of used oil before and after adsorption process using untreated and acids-treated RHA

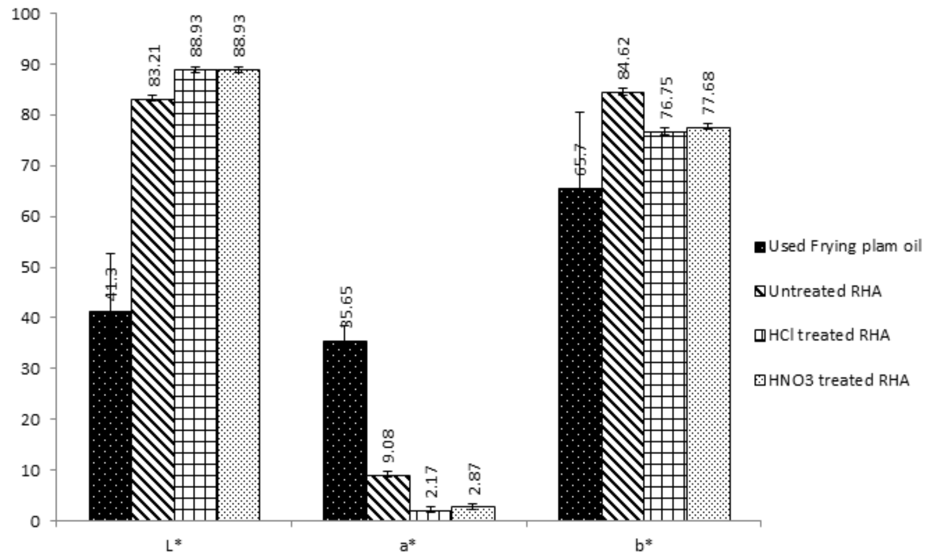

Figure 2 Color (L* a* b*) of used oil before and after adsorption process using untreated and acids-treated RHA.

The TPC value in original used oil was 10.17%. It was reduced to 7.87% (23.60% reduction) after adsorption process using untreated RHA and even reduced to higher levels using both acids-treated RHA of HCl (4.39%, 57.97% reduction) and HNO_3 (4.17%, 59.56% reduction) treated RHA.(Figure1 and Table1). Gholizadeh *et al.* (2013) reported that acid leaching of rice husks with HCl caused the higher SiO_2 content, lower alkali content, smaller particle size, and larger surface area in comparison with non-acid treated husks. These characteristics improved the performance of rice husk to adsorb polar compounds in used oil more than non-acid treated husks. Regarding to The Notification of Ministry of Public Health, Thailand, the standard accepted values of PV and TPC of frying oil are less than 10 meq./kg and 25% respectively.

Color of L^* a^* and b^* value in original used oil was 41.3, 35.65 and 65.7 respectively. L^* value was increased to 83.21 after adsorption process using untreated RHA and even increased L^* value significant (p<0.05) higher by using both acids-treated RHA of HCl (88.93) and HNO_3 (88.93) treated RHA. However a^* and b^* value after using HCl treated RHA (a^* 2.17 and b^* 76.75) and HNO_3 treated RHA(a^* 2.87 and b^* 77.68) showed significant (p<0.05) lower than using untreated RHA (a^* 9.08 and b^* 84.62)(Figure2). All the color values of used oil after adsorption process using both acids-treated RHA were significantly (p<0.05) improved color of used palm oil compared to untreated one. Chang *et al*. (2001) bleached of sesame oil with rice hull ash and found that the bleaching efficiency increased with ashing time from 300 to 500°C. It reached a maximum of 33.7% bleaching efficiency at 500°C.

The viscosity of the original used oil was 58.57cP.The HNO_3-treated RHA provided the lowest (55.29 cP,6.93% reduction) viscosity of used oil, followed by HCl-treated RHA (56.40 cP, 5.13% reduction) and untreated-RHA (57.95 cP, 2.58% reduction) as shown in Figure1 and Table1.It meant that both untreated and acids-treated RHA slightly improved the viscosity of used oil.

CONCLUSION

The rice husk ash prepared from acids treatment (HCl and HNO_3) and untreated one had their own specific capacity to recovery quality of used palm oil. The both acids treatments of RHA provided no difference of recovery used oil. They had significantly higher abilities to reduce total polar compounds and made brighter color compared to the untreated RHA. However, the untreated ash seemed to provide significant *(p<0.05)* better in reducing PV and FFA contents. Rice husk ash even in untreated or acids-treated forms could be an appropriate adsorbent to improve the quality of used palm oil.

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