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ScienceDirect
Separation and Purification Technology 56 (2007) 257–264
Separation Purification Technology
www.elsevier.com/locate/seppur

Variation of peroxide value in water-degummed and alkali-refined soy oil during bleaching under vacuum

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Received 12 September 2006; received in revised form 30 January 2007; accepted 31 January 2007

Abstract

Variation of peroxide value in water-degummed and alkali-refined soy oil during bleaching using regenerated clay under vacuum was investigated in this study. Experimental results indicated that the rate of reduction of dimensionless peroxide value increased with an increase of ratio of clay/oil or bleaching temperature. The rate could also be increased by decreasing bleaching pressure, particle size of clay or water content of clay. Initial peroxide value and agitation speed, however, were found to have no influence on the reduction rate. Furthermore, an empirical relationship between dimensionless peroxide value and bleaching time was determined. Regenerated clay produced in this work was found to be more efficient than activated clay in reducing peroxides.

Keywords: Bleaching; Peroxide value; Regenerated clay; Soy oil; Vacuum

1. Introduction

Peroxides in edible oil may reduce the stability [1] and the flavor score [2] of the oil and are normally removed in the bleaching step by an adsorbent. Hence, the removal of peroxides in oil is an important step in an oil refinery process. Several reports on the peroxides removal from soy oil have been found [3–13]. The mechanism of the variation of peroxides [3–6], the effects of type [7–11] and the dosage [9,12,13] of adsorbent used, the bleaching temperature [3], the water content of oil [3] as well as the bleaching time [3] on the peroxides removal have been the focus of previous studies.

To understand the kinetics of the bleaching, a study on the effects of bleaching atmosphere, particle size of clay, water content of clay, initial peroxide value, ratio of clay/oil, agitation speed and bleaching temperature on the rate of variation of peroxide value in water-degummed and alkali-refined soy oil has been performed and an empirical rate equation of the reduction of peroxides has been determined [14]. In the above study [14], bleaching was carried out under nitrogen stream, since its removal efficiency of the peroxides has been found to be higher than that under vacuum. However, commercial bleaching is normally carried out under vacuum. To be close to the commercial operation conditions, the bleaching experiments performed in this study are under vacuum of 50 mmHg [1]. In a continuation of the former study [14], the effects of same operation parameters excluding the bleaching atmosphere, which has been replaced by bleaching pressure, on the rate of the reduction of peroxides are studied in this investigation. An empirical rate expression of the reduction of dimensionless peroxide value is also determined and compared to that under nitrogen stream. The rate equation determined is thought to be helpful to designing and operating the industrial bleaching vessel.

2. Experimental

2.1. Materials

Compressed air and nitrogen gas (Yuan-Ron, Taipei, Taiwan) with a minimum purity of 99.99 and 99.55%, respectively, were employed. Reagent grade of acetic acid, isooctane, potassium iodide, sodium thiosulfate, and sulfuric acid were all supplied by Acros Organics (Geel, Belgium). Water-degummed and alkali-refined soy oil, deodorized soy oil, the spent clay and the activated clay (Optimum 230FF, P.T. Süd-Chemie Indonesia) were donated by the TTET Union Corporation (Tainan, Taiwan). Soy oil prior to bleaching was flown over by 3 mL/s nitrogen stream to protect it from being oxidized.

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doi:10.1016/j.seppur.2007.01.038

2.2. Regeneration of spent clay

Regeneration of spent clay was carried out in a box furnace (VT-10, Kinghwang, Taipei, Taiwan). It was heated up from room temperature under an air stream (5 mL/s). When the furnace was raised to 500 °C and had been maintained there for 30 min, 20 g of spent clay loaded in an alumina boat (16 cm × 4 cm × 2.1 cm) was placed into the furnace for 50 min. It was then removed and cooled in a nitrogen stream. The regenerated clay thus obtained was then sieved by Tyler standard screens into four batches of samples with different sizes: 350 mesh/400 mesh (38.5 μm); 270 mesh/325 mesh (48.3 μm); 230 mesh/270 mesh (57.3 μm) and 140 mesh/200 mesh (88.1 μm). These samples were then stored separately in stoppered bottles. The compositions and physical properties of activated clay and regenerated clay used were determined by the following instruments: inductively coupled plasma-mass spectrometer, ICP-MS (model Sciex Elan 5000, Perkin-Elmer, Wellesley, Massachusetts, USA), X-ray diffractometer (model Rotaflex Ru-200B, Rigaku, Tokyo, Japan), scanning electron microscope (model JSM-6500F, JEOL, Tokyo, Japan), surface area analyzer (model BET-202A, Porous Materials Inc., Ithaca, New York, USA), density meter (model Accupy 1330, Micromeritics, Norcross, Georgia, USA), moisture determination balance (model MB-200, Ohaus, Florham Park, New Jersey, USA) and pH meter (model AT-200, Kyoto, Kyoto, Japan).

2.3. Bleaching of water-degummed and alkali-refined soy oil

Bleaching experiments were performed in a 300 mL vacuum flask with three necks. A valve in one of the necks is designed to control the feed of regenerated clay. One hundred millilitres of water-degummed and alkali-refined soy oil was poured into the flask and predetermined amount of regenerated clay was stored in the neck above the valve prior to bleaching. The oil in the flask was stirred by a magnetic stirrer and heated to the desired temperature by an oil bath. At the same time, a vacuum was maintained in the system by a mechanical pump during the heating period and the consequent bleaching process. It took 15–20 min to reach the desired temperature. As the oil temperature reached the desired level and was maintained at that point for several minutes, the valve on the feeding neck was opened to drop the clay into the oil agitated by a stirrer. The bleaching then started isothermally. After a preset time, the bleaching was stopped by replacing the oil bath with a bath of ice and water. After cooling to 25 °C, the slurry was filtered by a Toyo 5C filter paper and a sufficient amount of filtered oil was collected to determine the peroxide value. The bleaching conditions are depicted in Table 1. The italic values shown in the table are the standard operating variables. That means when the effect of that variable was not studied, it was held at this value in that series of experiments. These values are: bleaching pressure, 50 mmHg; particle size of clay, 38.5 μm; water content of clay, 8 wt%; initial peroxide value, 10.51 meq/kg; ratio of clay/oil, 0.005 g/g; agitation speed, 600 rpm and bleaching temperature, 100 °C. Erickson [1] pointed out that the bleaching conditions for the commercial processes are bleaching pressure, 50 mmHg; ratio of clay/oil, 0.003–0.006 g/g; bleaching temperature, 100–110 °C and bleaching time, 20–30 min. Therefore, the ranges of the operating variables are selected close to these values.

Table 1
Values of operation variables for bleaching experiment

Variable	Value[a]			
Bleaching pressure (mmHg)	20	*50*	100	150
Particle size of clay (μm)	*38.5*	48.3	57.3	88.1
Water content of clay (wt%)	3	*8*	14	20
Initial peroxide value (meq/kg)	5.7	7.22	9.48	*10.51*
Ratio of clay/oil (g/g)[b]	0.004	*0.005*	0.006	0.007
Agitation speed (rpm)	150	300	*600*	800
Bleaching temperature (°C)	80	90	*100*	110

[a] Italic values are standard operation variables.
[b] The weight of clay is on dry basis.

Three experimental runs were conducted under the same experimental conditions and the average value was used.

2.4. Determination of peroxide value in soy oil

The peroxide values in the oil before and after bleaching were determined by AOCS Official Method Cd 8b-90 [15] except that $Na_2S_2O_3$ of 0.01N, instead of 0.1N, was used as the titrant. These values were determined immediately after bleaching to prevent oxidation of the oil.

The dimensionless peroxide value, which will be presented later, is defined as C/C_o, where C and C_o are the peroxide values in meq/kg at $t = t$ and $t = 0$, respectively.

3. Results and discussion

3.1. Content and physical properties of activated clay and regenerated clay

The composition and physical properties of activated clay and regenerated clay determined are listed in Tables 2 and 3, respectively. It is seen that the content and physical properties of these two clays are close to each other. The interesting finding from Table 3 is that the specific surface area of the regenerated clay is higher than that of the activated clay. This result can

Table 2
Content of silicon and metallic ingredients of activated clay and regenerated clay (wt%)

	Si	Fe	Al	Ti	Ca	Mg	Ba	Cu	Cr	Ni
Activated clay	15.76	2.31	3.42	0.61	0.39	0.41	0.0097	0.0021	0.0018	0.0004
Regenerated clay	16.72	2.43	3.46	0.63	0.27	0.50	0.0091	0.0050	0.0019	0.0009