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DECOLOURIZATION AND DEODOURIZATION OF SOYABEAN OIL: A REVIEW

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ABSTRACT

Crude fats and oils contain varying quantities of impurities such as phosphatides, mucins, free fatty acids, dyes and substances which affect the odour and colour. These impurities are removed at various steps in the conventional chemical refining, which includes degumming, neutralization, washing, drying, bleaching, filtration, and deodorization. Degumming is done to remove phosphatides. Hydratable Phosphatides can be precipitated by adding water to the oil, nonhydratable phosphatides must be destroyed by adding acids. Free-fatty acids are removed by neutralization with alkali hydroxides leading to soaps which can be removed. Undesirable coloured impurities are removed by bleaching with an adsorptive reagent. The undesirable compounds are adsorbed and can be removed together with the adsorbent by filtration. The last step is deodourization and by this step undesirable volatile and odoriferous materials are removed. During decolorization and deodorization process many antioxidant get lost. Soyabean oil contains luxury antioxidants like tocopherols, flavonoids, ascorbic acid, carotenoids, phytosterols. Brief of many literature reviewed is as follows -
Pryor *et al.* (1985) invented that color bodies and phospholipids can be removed effectively form soya oil by treatment with high surface area amorphous silica composition having an acid supported there on. L1ST *et al.* (1989) studied about "Colour removal and Oxidative Stability of soybean Oil Extracted with Supercritical Carbon Dioxide at 50C and 8,000 psi .Moulton *et al.* (1999) applied Continuous Ultrasonic Degumming of Crude Soybean Oil to remove gums which contributed in colour and odour of Soyabean oil. Bortolomeazzi *et al.* (2000) studied dehydration of sterol by phosphoric acid during refining process which is also responsible for colouring and odouring of soyabean oil. Díaz *et al.* (2001) studied of acid activation clay for decolorizing vegetable oils. Kondal (2001)Decolourization of soya oils by membrane Process. Wang *et al.* (2002) studied preparation of decolourization and deodourization of stable Long-chain polyunsaturated soyabean oil by biomass. Carrin *et al.* (2003) process for deodorizing of soyabean oil by principal of continuous countercurrent falling film stripping steam distillation. Moore *et al.* (2003) invented modified physical refining of soybean oil having high calcium and/ or magnesium. Cert *et al.* (2003) discovered formation of stigmasta-3,5-diene in soya oils which affect odour of oil. Koivu *et al.* (2005) using a biotechnology approach to increase oil content of soya oil.
Manjula *et al.* (2006) invented process for Soya oil decolourizing and deodourizing in submerged membrane bioreactor in which loss of enzyme is reduced. Yoshida *et al.* (2006) invented MGO (magnesium oxide) Impregnated activated carbon and its use in an improved soya oil. Bray *et al.* (2006)

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activated carbon improved vegetable oil refining process. Valli *et al.* (2009) studied on effects of heating on odour soya oils and their blends: Focus on modifications of phenolic fraction. Omar *et al.* (2009) found carbonaceous materials from seed hulls improve bleaching of vegetable oils Petron *et al.* (2010) refining of soya oil by isothiocynate .

INTRODUCTION

Crude fats and oils contain varying quantities of impurities such as phosphatides, mucins, free fatty acids, dyes and substances which affect the odour and Colour. These impurities are particularly undesirable in fats and oils used as foodstuffs (Erickson *et al.* 1980). It contains Inorganic impurity like Calcium, Magnesium , Iron etc. It has organic impurity like Oleic acid, Glycerol, Monooleates , Chloro phenol etc. (Cert *et al.* 1993). It has Toxic impuritychlorinated dibenzo-p dioxin , TCDD etc. During decolorization and deodourization process many such antioxidant get lost, so one should maintain balance between percent of antioxidant and refining process.

These impurities are removed at various steps in the conventional chemical refining, which includes degumming, neutralization, washing, drying, bleaching, filtration, and deodourization. According to Francisco *et al.* (2001) degumming is done to remove phosphatides. Hydratable phosphatides can be precipitated by adding water to the oil; nonhydratable phosphatides must be destroyed by adding acids. Free-fatty acids are removed by neutralization with alkali hydroxides leading to soaps which can be removed. Undesirable coloured impurities are removed by bleaching with an adsorptive reagent. The undesirable compounds are adsorbed and can be removed together with the adsorbent by filtration. The last step is deodorization and by this step undesirable volatile and odoriferous materials are removed.

Soybean seeds contain luxury, excellent nutritional ingredients benefiting human health. Some food products of soybean seed, i.e., soybean flour and soybean oil, are evidenced to have the antioxidant activities (Jung, *et al.* 2003). Isoflavone glycosides and their derivatives, phospholipids, tocopherols, amino acids, and peptides, are found in soybean flour. During decolorization and deodorization process many such antioxidant get lost, so one should have maintain balance between the percentage level of antioxidant during refining process.

Common process for crude vegetable oil refining is given in Figure 1.

Industrial process

Industrial process for decolourization and deodourization of Soyabean oil takes place in following steps-

Pretreatment, Degumming, Neutralization, Water Washing, Bleaching by fuller earth and Deodorization.

Pretreatment

In pretreatment process, water is the sole degumming agent; the phosphorus content is 650 p.p.m, which corresponds to phospholipids content of 1.95%.it is then pumped through a line at a rate of 30,000 pound per hour. Water is metered into this line as water flow controller at a rate of 1.0% or 300 pound per hour. The analysis of wet gums is 33% of water, 45% of phospholipids and 22% of soyabean oil. The wet gums oil then further processed to make oil commercial lecithin. The yield of partially degummed oil is 98% on dry weight basis.

Degumming

Degumming removes various mucilaginous products, primarily protein or albuminoid substances and phospholipids, from the crude vegetable oil. These phospholipids, primarily lecithin, cephalin and inositol phosphatide, are primarily responsible for the rather strong and bitter flavor and aroma of the crude oil.

The degumming process consists of adequately mixing with the crude vegetable oil, an organic acid such as phosphoric acid or acetic acid, followed by a little water; the resulting hydrated, mucilaginous globules are subsequently removed from the oil by centrifuging. While substantially all of the phospholipids should be removed, to a level at least below 2.0 p.p.m., as phosphorus unless substantially all of the phospholipids are thus removed, a dark colored oil will be produced by decomposition of the remaining phospholipids at the elevated temperatures encountered during the final step of vacuum steam stripping and deodorizing.

The preferred method of degumming for use in the

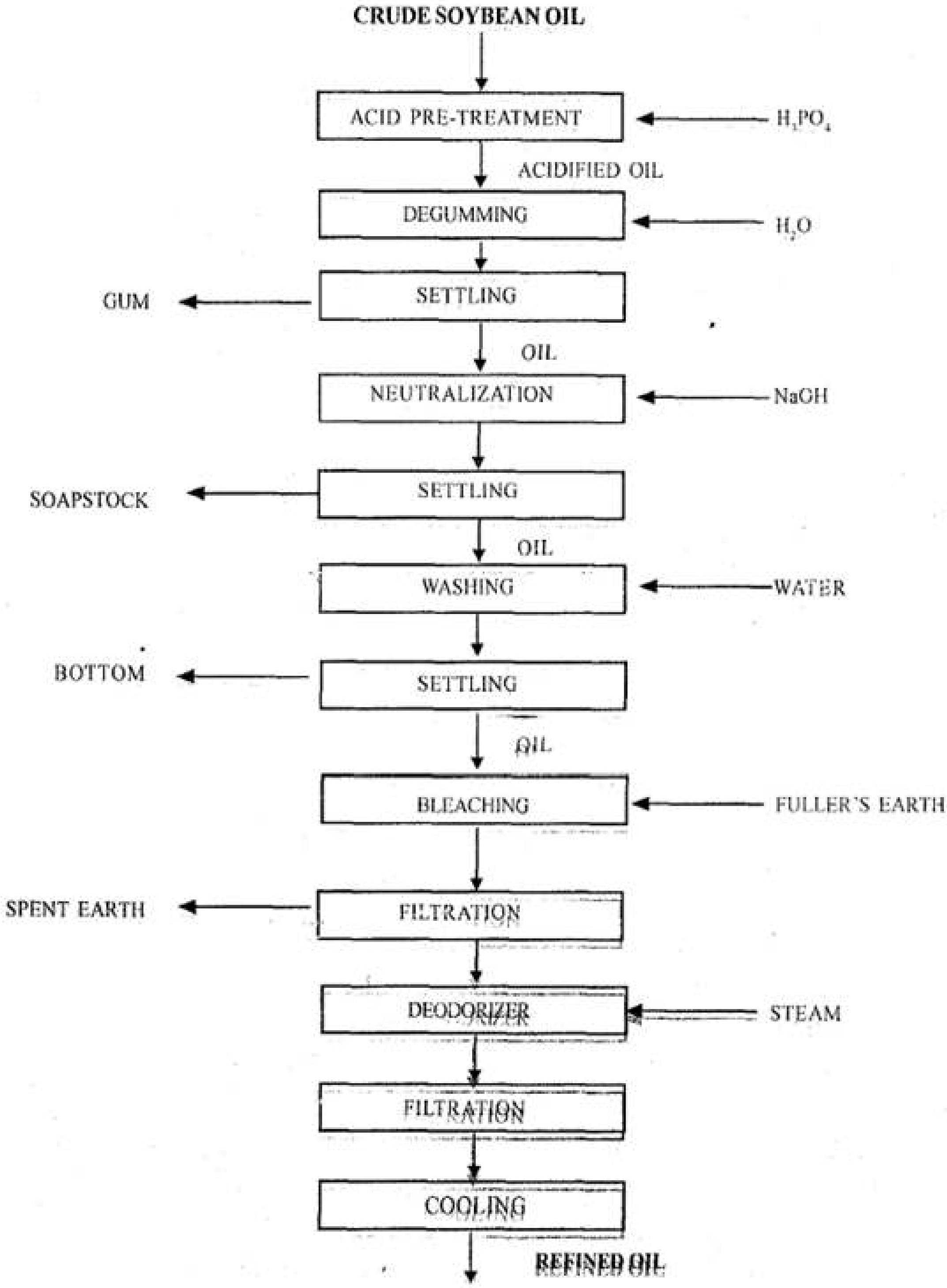

Fig. 1 Flow chart -refining process for crude soybean
(Source - Method of refining liquid fats and oils Bock - November, 1997 – 3354188)

improved refining process of the present invention is one by a continuous process. An acid such as 85% phosphoric acid is use before the addition of the water. The amounts used may vary from 300 to 2,000 p.p.m. by volume of oil. The amount of water may be from 1.0 to 3.0% by volume.

The mixture is introduced into a continuous centrifuge in which it is heated and caused to circulate continuously, whereby the mucilaginous products are completely hydrated and the aqueous phase containing these hydrated mucilaginous products is finally discharged.

Gums from the degumming step contain: Phospholipids, Carbohydrates, Proteins, Metals, Soaps, Water, Small parts of free fatty acid.

Bleaching

Bleaching is carried by either Fuller Earth or Activated Carbon reagent. The impregnated activated carbon treatment of the present invention reduces the phospholipids and free fatty acid concentration of the degummed oil sufficiently to result in a final product which is satisfactory as a consequence of the removal of other impurities in the oil, especially peroxide compounds, by the impregnated activated carbon treatment step. It is known to employ activated carbon conventionally as a bleaching agent that is as a decolorizing agent to remove various pigment products. When employed as a bleaching agent, the activated carbon is typically utilized in powder form in a batch or continuous batch-type operation.

In accordance with the improved refining process by activated carbon of the present invention, it is possible to eliminate two conventional refining steps such as Neutralization and water treatment. Therefore activated carbon method reduces power consumption. This is extra added advantage.

Neutralization

Neutralization refers to neutralization of fatty acids in the feedstock by reaction with caustic soda followed by separation of the resulting soapstock from the oil. This step not required in Activated Carbon step.

Neutralization is accomplished simply by treating the oil with an aqueous solution of sodium hydroxide or other strongly alkaline reagent. The free fatty acids in the oil, generally present in amounts of from 0.5 to 3.0% by weight, are removed as precipitated soaps produced by the reaction of the fatty acids and alkaline reagent. The soap thus formed may be removed by centrifuging and the separated soapstock disposed of in in the same manner. Theses soapstocks are acidulated and free fatty acids are recovered.

The problem is, however, that the caustic also saponifies small amount of neutral oil, which results in direct product losses. Additional losses are caused by emulsions between them as well as between neutral oil and wash water.

This leads to costly increases in bleaching earth and catalyst consumption if the oil is to be hydrogenated and ultimately results in an unacceptable finished product , soybean oil with 10 ppm residual phosphorous after neutralization may, for example, requivalent to a neutralized oil with 5 ppm phosphorous. Furthermore, it may not be possible to reduce residual phosphatides and other impurities by increasing the amount of bleaching earth.

Proper by designed plants, are capable of reducing the free fatty acids in the crude oil to an acceptable level of not more than 0.05% .

The neutralized oil is heated to about 90°C and mixed with 10-15% hot process water, after which the oil goes to the second separator, where the soapy water is removed to a residual amount of less than 70 ppm soap. If lower levels are desired, food - grade acid can be added to the water to improve separation or after the separator to split residual soap.

Deodourization

The next step in the convention refining is deodourization .During this step live steam is passed through the vegetable oil while it is maintained under a high vacuum and at elevated temperature. The temperature range from 460 to 530 °F and the vacuum is maintained at 4 to 6 mm hg. The process may require from one to one half to seven hours. During the process most of the FFA remaining in the vegetable oil are distilled off. Most of the remaining pigment product are destroyed during this step as well. The acid value and color of the oil are thus improved and the odor and flavor are made acceptable. However if any appreciable phospholipids remains the elevated temperature experienced during this step would result in a darkening of the oil.

Literature review

Pryor *et al.* (1985) invented that color bodies and phospholipids can be removed effectively form soya oil by treatment with high surface area amorphous silica composition having an acid supported there on. It has been found that presence of a strong acid in the pores of the silica adsorbent greatly improves ability to remove chlorophyll, reds as well as yellow color. The inherent property of amorphous silica to adsorbed phospholipids is not lost compromised by acid treatment described herein. The composition described utilize amorphous silica on which acid has been supported in such a manner that least portion of acid is retained in pores of silica.

The studied prove that crude oil extracted from soya flakes with supercritical carbon dioxide (CO2,) is characterized for least color, free fatty acid, phosphorus, neutral oil loss, unsaponifiable matter, tocopherol and iron content and compared to a commercial hexane-extracted sample of crude degummed oil. Characterization and processing studies indicate that extraction yields a product comparable to a hexane-extracted degummed oil List *et al*. (1989).

Moulton *et al*. (1999) applied ultrasonic energy to continuous degumming for the efficient removal of phospholipids from crude soybean oil. The crude oil and water (2.0% by weight) were pumped through an ultrasonic processing cell, oil and hydrated gums were separated by centrifugation and the recovered oil was vacuum bleached. The degummed and bleached oil had a residual phosphorus content of less than 10 ppm and was subsequently deacidified-deodorized in all-glass laboratory deodorization equipment. Odor and flavor evaluation indicated that the salad oil produced by the process of ultrasonic degumming deodorization-deacidification was equivalent in quality and stability to a conventionally processed oil.

Bortolomeazzi *et al*. (2000) studied dehydration of sterol by phosphoric acid during refining process which is also responsible for colouring and odouring of soyabean oil.The dehydration of sterols during the refining process of vegetable oils results in the formation of steroidal hydrocarbons (sterenes or steradienes) with two double bonds in the ring system. Other steroidal hydrocarbons whose structures were in agreement with the presence of three double bonds in the ring system were detected in the sterene fractions of refined vegetable oils.

The more recent studies on the acid activation of Brazilian smectitic clays for decolorizing vegetable oils. The best known property of bleaching earth is its high adsorption capacity, which can be enhanced by acid treatment. The increase in specific surface area and pore volume improves the adsorption capacity of metal impurities, phosphatides and color bodies. However, the mechanisms of impurity removal are not always simple and other properties, such as cation exchange capacity (CEC), as well as acid and catalytic properties must be taken into account. Díaz *et al.* (2001).

Kondal (2001) studied membrane decolourization studies of chlorophyll added soya oil were conducted in a batch membrane cell using two polymeric composite membranes(NTGS-2100 AND NTGS-1100),and one polyethylene micro filtration membrane(pe-1100).NTGS-2100 membrane could remove up to 96% and 72% chlorophyll from the undiluted oil solution, respectively. Permeate oil flux was very low when undiluted oil was used as feed , but improved many fold by diluting with hexane.NTGS-1100 membrane gave higher permeate flux compared to NTGS-2100, but showed reduced rejection. Absorbance spectra of crude Soyabean oil and the permate in the 350-550 nm range showed a greater degree of decolourization by polymeric composite membranes.pe-30 membrane Showed insignificant rejection of color compound. Carrin *et al*. (2003) invented process for deodorizing of soyabean oil by principal of continuous countercurrent falling film stripping steam distillation.

The invention relates to the deodorizing and/or physical refining of high-boiling organic edible oils, fats and esters according to the principle of continuous countercurrent falling film stripping steam distillation in an externally imposed temperature field. For this purpose, the present invention provides a novel process and a novel apparatus for carrying out the process.

In particular, the invention relates to a process of deodorizing and/or physical refining of high-boiling organic edible oils, fats and esters, wherein the liquid heated to a temperature ranging between 220 ^{O}C and 280 ^{O}C, at a working pressure ranging between 2 and 10 mbar, flows down as a thin film having a film thickness of less than 1.0 mm at the wall of surfaces which substantially are disposed vertically, which define trickle passages and of which at least a part is maintained at a higher temperature than the flowing down liquid, and wherein vapor of a low-molecular liquid, preferably steam, is directed through these trickle passages in countercurrent.

A process for treating crude soybean oil containing calcium and magnesium obtained from soybeans by mechanical extraction comprising: a) mixing the crude soybean oil with water or an acidic aqueous solution to form gums of hydratable phospholipids; b) separating the gums from the crude oil to obtain first treated soybean oil; c) intimately mixing the first treated oil with a basic aqueous solution to produce soapstock containing calcium and magnesium, whereby the amount of calcium and magnesium remaining in the oil is less than 100 ppm; and d) separating the soapstock from the first treated soybean oil Moore *et al.*. (2003).

Cert *et al.*. (2003) found formation of stigmasta-3, 5-diene in soya oils which affect odour of oil. The formation of stigmasta-3,5-diene (STIG) in vegetable oils from beta-sitosterol affect odour of Previously, analytical methods for STIG determination were developed and verified. For virgin olive oil and crude vegetable oils, the usual oil production processes (pressure, centrifuging and solvent extraction) and long term storage did not produce measurable amounts of STIG, except in the case of crude olive pomace oils where small quantities aroma as a result of the high temperature applied to the solid residues during the drying operation. The influence on STIG generation of variables affecting the refining processes was studied. Although minor amounts of STIG appeared after only heating the oil, this compound was produced mainly during the bleaching earth treatment. The decolourtion temperature and the bleaching earth activity were the most important variables involved in STIG formation. After deodourising, carried out under normal conditions, the refined olive oils retained measurable amounts of STIG. The refining of other vegetable oils with high beta-sitosterol content (such as sunflower, rapeseed and soya oils) also rendered considerable amounts of STIG. These results support the method based on STIG determination for detecting low percentages of refined vegetable oils in soya oils and crude seed oils.

Lipid hydroperoxides (LOOH or oxidized oils) are known as unfavorable food components. Molecular details of the fate and mechanisms of LOOH to exert adverse effects in vivo are, however, little understood. In the present study, we demonstrated that LOOH generated alkylperoxyl radical (LOO\cdot) after reaction with various compounds such as myoglobin, cytochrome c, hemin, hematin, etc., but little formation of other radical species was noticed such as (L\cdot or LO\cdot). It was also shown that (LOO\cdot) thus formed exhibits cytotoxicity and caused DNA damages including strand breakage and a basic site formation. This highly toxic (LOO\cdot) is effectively scavenged by hot water extracts of vegetable (soup), flavonoids, polyphenols as well as tocopherols. Another important finding is that crude vegetable oils are rich in potent- LOO\cdot scavenging activity, which exhibits potent anti-oxidant activity as well; whereas highly purified oils are scanty in such components and LOO\cdot scavenging activity. These findings imply that a considerate processing in the refining of oils should be needed to retain such potent endogenous anti-oxidative radical scavenging-components (Bera *et al.* 2004).

Continuous hydrolysis of soya oil by *Candida rugosa* (CRL) lipase was studied in a two configuration of microporous hydrophilic membrane bioreactor. This two confuguration of module side stream and submerged membrane bioreactors is based on the separation of enzyme and products (or substrates) by a semipermeable membrane that creates a selective barrier. Permeable solutes can be separated from the reaction mixture by the action of a driving force (chemical potential, pressure, electric field) that is present across the membrane. A complete retention of the enzyme within the system is the first and most important requirement for a successful continuous operation of a membrane bioreactor. Upon this retention, the enzyme becomes confined to a defined region of the membrane reactor, where reaction with the substrate occurs. The enzyme was immobilized on the shell side of the membrane and is usually entrapped inside the pores of membrane matrix (Manjula *et al.* 2006).

Yoshida *et al.* (2006) invented MGO (magnesium oxide) impregnated activated carbon and its use in improved process for making refined oil. The decolorization of soya oil or degummed of soya crude oil and removing organic acid there from .The improved process of the present invention for making soya refined oil comprise the step of degumming process. Passing the degummed oil through a bed of granular activated carbon with from about 1% to 15% By weight of MGO and subjected and treated oil to steam distillation at reduce pressure.

In accordance with the improved refining process by activated carbon of the present invention, it is possible to eliminate two conventional refining steps such as Neutralization and water treatment. despite the eliminated steps, the end product refined Oil is acceptable with respect to prevailing industry standards for taste, odor and color. This conventional step elimination is possible because activated carbon treatment reduces phospholipids and FFA up to acceptable limit and is, moreover, storage stable. Therefore activated carbon method reduces power consumption. This is an extra and added advantage.

The Phenolic profile of two different virgin soya oils and their admixture in different percentages have been analyzes after heating treatment by microwave or conventional oven. Changes in the Phenolic profile upon heating were evaluated by chromatographic and spectroscopic method also monitoring the antioxidant activity by ABTS Test 3,4-DHPEA-EA, P-HPEA-EA, and EA showed the highest decreases after thermal treatment . the only compound that showed a lear increase with heating , in particular by convential oven, were the dialdhydic form of elenolic acid(EDA) and p-hydroxyphenylethanol linked to the dialdehydic form of elonic aid(p-HPEAEDA). A compaision between the variations afer heating of the sum of monoaldehydic and dialdehydic forms of phenolic compounds obtained by using different analytical approaches (HPLC-DAD/MSD and 1D and 2D NMR spectroscopy) was made. The results showed a good agreement of these two high-resolution techniques. Valli *et al*. (2009)

Omar *et al*. (2009) found carbonaceous materials from seed hulls improve bleaching of vegetable oils . Seed hulls, namely cottonseed, peanut, sunflower, soybean, faba bean and lupine were evaluated as carbonaceous materials for the bleaching of crude soybean oil. The six seed hulls were activated by carbonization, steam activation and acid activation. Two reference standards, Fullers earth and Tonsil clay, were used for comparison throughout the whole study. Bleaching of crude soybean oil under vacuum at 100 °C using the treated hulls was carried out. The effect of bleaching with the different hulls on the oil characteristics was evaluated by determining the % free fatty acid, % reduction in peroxide value,%removal of phospholipids, % bleachability and oxidative stability of the bleached oils. Results revealed that bleaching with carbonized hull yielded oils with least free fatty acid content and highest oxidative stability. Bleaching with acid activated hull carbons gave oils with least content of peroxides, phospholipids together with best olor. Acid activation of the hulls resulted in highest increase in surface area, pore volume and least pore dimension.

Petron *et al*. (2010) studied novel two step synthesis of soy oil based isothiocyanate. Allylicaly brominated soybean oil (ABSO) was reacted first with ammonium thiocyanate in tetrahydro furan to form allylic thiocyanates. These compounds were then converted to isothiocyanated soybean oil (ITSO) by a thermal rearrangement. Conversion was found to be 70%. The structure of the ITSO was characterized by IR and 1 H-NMR techniques. Then ITSO was reacted with ethylene glycol, glycerol, and castor oil to produce polythiourethanes and ethylene diamine and triethylene tetra amine to produce polythioureas. Thermal properties of the products were determined by DSC and TGA techniques.

CONCLUSION

Crude soyabean oil contain varying quantities of impurities such as phosphatides, mucins, free fatty acids, dyes and substances which affect the odour and colour. These impurities remove by number of process based on adsorption. Here we consider two types of adsorbing agent like fuller earth and activated carbon.

After review of literature it is conclude that activated carbon as adsorbing agent we get almost same result as get in Fuller earth adsorber, however neutralization and water washing step is by pass in Activated carbon process. Hence in Activated carbon process there is saving in valuable chemical, saving in power, saving in time.

Ultrasonic degumming method proved lower phosphorus content of the degummed oil. Degumming with ultrasonic is five time faster than traditional process.

A membrane process offers several advantages over the conventional method of oil refining. Conceptually, membranes could be used in almost all stages of processing. In the present review, various attempts made by the researchers towards degumming, dewaxing, deacidifying, and decolorizing edible oils using membrane technology.

The future research bleaching by activated carbon paths would include shows that better removal of color and odour and optimizing the refining technology of industry process to minimize the loss of beneficial phytosterols and other antioxidant and also save Power.

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