CHAPTER 1
INTRODUCTION

1.1 Rationale /Problem Statement

In recent years there has been increasing interest in the health and nutritional aspects of rice bran oil as well as in its use as industrial oil. Natural rice bran oil has many constituents which are considered to provide good health benefits (Xu and Godber, 2001). It contains 4.2% unsaponifiable matter, which includes antioxidants and micronutrients, compared to <1-2% in other oils. The unsaponifiable matter is rich in tocopherols and tocotrienols, gamma oryzanol, phytosterols, polyphenols and squalene (Sugano and Tsuji, 1996). These antioxidant compounds have beneficial roles in lowering cholesterol levels, as well as in the prevention of cardiovascular diseases (Lloyd et al., 2000). Tocopherols are believed to have anticancer effects (Tarber and Packer, 1995; Dunford, 2001), and oryzanols are believed to have cholesterol-reducing effects (Nicolosi et al., 1991; Rukmini and Raghuram, 2000).

The typical composition of crude rice bran oil is 81-84% triacylglycerols (TAG) 2-3% diacylglycerols (DAG), 1-2% monoacylglycerols (MAG), 2-6% free fatty acids (FFA), 3-4% wax, 0.8% glycolipids, 1-2% phospholipids (PL) and 4% unsaponifiable matter (Hvolby, 1971). However, the oils are commonly highly colored as a result of the presence of impurities, such as chlorophyll, carotenoids, xanthophylls and oxidized products (Park and Ming, 2004), that are considered objectionable to consumers. Moreover the presence of large quantities of these pigments reduces the shelf life of rice bran oils. Thus, the oil needs to be bleached, although the presence of the relatively large quantities of these impurities makes the bleaching of rice bran oil more difficult than for most other vegetable oils (Cowan, 1976).

The bleaching process in the refining of any vegetable oil reduces oil colour values and other unwanted compounds by adsorptive purification using an adsorbent. Many types of adsorbent, including activated clays, activated carbon and silica based products, have been investigated for the removal of pigments from vegetable oils (Proctor and Synder, 1988; Proctor and Palaniappan, 1990; Habile et al., 1992; Kamga et al., 2000; Falaras et al., 2000), but acid-activated montmorillonite is the most commonly used adsorbent in vegetable oil bleaching (Srasra et al., 1989; Sarier and Güler,1988; Christidis et al. 1997; Falaras et al., 2000; Christidis and Kosiari, 2003), because of its low cost and high efficiency.

Although montmorilonite is the most important and widely used clay for the stabilisation of plant-based oils, colour removal and purification (Boukerroui and Quali, 2002; Gonzalez-Pradas et al, 1994), other clay minerals such as sepiolite (Sabah, 2007; Sabah et al., 2007), and attapulgite (Huang, et al; 2007) have been considered as alternative adsorbents for the oil refining process. However, few details have been documented in the scientific literature. Also, kaolin is another clay mineral with high surface area that has not previously been studied as an adsorbent for vegetable oil bleaching.

The kaolin group minerals, commonly referred to as China clay, are hydrated aluminosilicates, with a general chemical composition Al_2O_3: SiO_2 : H_2O = 1:2:2: or $2SiO_2.Al_2O_3.2\ H_2O$ per unit cell. Structurally they are 1:1 type phyllosilicates in which sheets of alumina octahedra are combined with silica tetrahedral sheets. These sheets extend continuously in the *a* and *b* directions and are stacked one above the another in the *z* or *c* direction (Tan, 1993). The various kaolin minerals, kaolinite, dickite, nacrite, and halloysite, are distinguished by these stacking arrangements. The asymmetry of the unit cell imparts a dipolar character to the interlayer region, with the ideal structure having the basal plane of oxygen atoms in one crystal unit lying opposite the basal plane composed of OH ions of the next layer. The unit layers are held together by hydrogen bonding, resulting in a large cohesive energy (Giese, 1988) and yielding an interlayer space with fixed dimension and only a very small cation exchange capacity.

Although, the mechanism of adsorption of cations on natural clays is governed by the cation exchange capacity of the mineral, adsorption of other molecules is influenced by various properties, such as surface area, surface charge, pH, etc. (Garcia, et. al. 1999; Matthes, et al., 1999). The adsorption capacity of clays can be increased by various physical and/or chemical treatments to modify structural (chemical composition, changes in interlayer distance, new species in interlayer position, etc.), textural (surface area, pore distribution, porosity, etc.), and/or acidic properties (Lewis and/or Bronsted sites). Modification of clays can be carried out by various methods, including intercalation of inorganic and/or organic substance, intercalation of hydrolysed inorganic OH-cation specie, pillaringclay, ligand intercalation, and acid treatment etc.

Thailand is the World's leading rice exporting country. Traditionally, the most valuable by-product of the rice milling industry, rice bran, was either discarded or used as only livestock feed. However, nowadays, Thailand produces rice bran oil from rice bran for local consumption and export to Europe and Asia. In the refining process, imported montmorillonite bleaching clay is currently used at considerable cost, although there are appreciable kaolin clay deposits that could potentially be developed for this purpose.

The present research project was designed to study and develop kaolin as an adsorbent for the oil refining industry in Thailand to be used as an alternative to imported montmorillonite bleaching clay. Kaolin has not previously been tested for purification of edible oils, so the initial aim of the work was to test the effectiveness of various modified kaolins as adsorbents for the oil refining process. A second objective of this work was the characterisation of the modified Thai kaolins using various physical and spectroscopic techniques to understand details of the properties of the Thailand clay samples. Since kaolin minerals are used in a wide range of local industries, ranging from building materials, paper making, pottery and ceramics, their physical, chemical and mineralogical properties have wider relevance than the adsorption processes investigated in the present project.

1.2 Research objectives

1.2.1 To determine the optimum conditions of kaolin modification for decolorisation of rice bran oil.

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1.2.2 To study the adsorption mechanism of pigments in rice bran oil by modified kaolin.

1.2.3 To characterize the structural properties of modified kaolin samples using modern physical and spectroscopic techniques.

1.3 Scope of research work

1.3.1 To study the combined effects of physical and chemical treatments on kaolin modification.

1.3.2 To study the physical and chemical properties of kaolin before and after modification.

1.3.3 To analyse the adsorption mechanism of pigments on modified kaolin.

1.4 The expected value of the research

1.4.1 Assessment of the potential value of modified kaolin for use in rice bran oil decolorisation.

1.4.2 Production of added value for kaolin minerals in Thailand by developing new uses.

1.4.3 Provide the oil refining industry with an alternative to using conventional bleaching clay for decolorisation of vegetable oil.