CHAPTER I

INTRODUCTION

At present, large quantities of fuel oils have been used in several applications such as automobiles, trucks, ships and factories. As a whole, fuel oils have to be taxed according to the government rate, which depends on the types and purposes of the fuel oils. Difference in taxation has caused the government to lose a lot of revenue by crookery, for instance smuggling of untaxed oil, mixing of high-rate taxed oil with low rate taxed oil, and mixing of hydrocarbon solvents to fuel oils.

To prevent these problems, marker systems have been suggested as means to identify brands of fuel and to monitor the tax classification of petroleum products. However, various drawbacks have existed, for example, quinizarin, which was used as a marker for heating oil in France, which suffers from the disadvantage of low solvent solubility [1]. Furfural was used as a marker for fuel oil in Germany, but it is unstable in certain oils, making it too difficult to detect after storage [2]. Azo dyes also have been developed for marking petroleum products, which could be detected by simply extraction with acid or basic reagent, when they were used to mark fuel at lower concentrations than the previous markers [3]. In recent years, there has been reported of various synthesized azo dyes to be used as markers. For example, those reported by Silapakampeerapap [4] and Thowongs [5] who synthesized marker dyes from the reaction of cashew nut shell liquid (CNSL) with nitro anilines and chloro anilines, respectively. Nevertheless, these marker dyes were proposed to be used as markers in gasoline and high-speed diesel at high treat rate (15-30 ppm). Subsequently, Suwanprasop [6] synthesized marker dyes from aniline derivatives and cardanol, which was obtained from partial purification of decarboxylated CNSL. These markers were added into gasoline and high-speed diesel at levels of 2 to 5 ppm. Although marker dyes from cardanol were effective, CNSL has not been produced commercially.

Linear alkylbenzene (LAB), which has a production capacity of more than 0.7×10^6 tones per year [7], gains considerable importance as starting materials for the synthesis of linear alkylaniline, which were the raw material for petroleum markers in this research. Since LAB is the mono alkylbenzene with 10-14 carbon atoms in the alkyl side chain, it can be synthesized to produce a marker, which can be dissolved completely in fuel oils. Moreover, LAB has a lower price, so it will provide the lower priced markers. These novel markers also increased the variety of material with which petroleum might be marked.

LAB was converted to linear alkylaniline by nitration and reduction reactions, respectively. After that, linear alkylaniline was synthesized as markers by 2 methods. First, linear alkylaniline was coupled with diazonium salt of aniline derivatives. On the other method, linear alkylaniline was converted to diazonium salt by diazotization reaction and was then coupled with aniline or phenol derivatives. These synthetic petroleum markers were added to petroleum products at low levels and were detected by appropriate basic extraction.

The objectives of this research

The objectives of this research are to synthesize markers from LAB for petroleum products, and to study the properties of markers, through both qualitative determination in field tests and quantitative determination in laboratory tests, including stability of markers in fuel oils.

The scope of this research

The starting material of this research is LAB. It is converted to linear alkylaniline by nitration and reduction reactions, respectively. The markers will be synthesized from linear alkylaniline by 2 methods. The first one is the coupling reaction of linear alkylaniline with diazonium salts of aniline derivatives, including *p*-nitro aniline, *o*-nitro aniline, 4-chloro-2-nitroaniline, 4-chloro-3-nitroaniline, 2-chloro-4-nitroaniline, 2-chloro-5-nitroaniline and 2-methoxy-4-nitroaniline. The second one is the coupling reaction of diazonium salt of linear alkylaniline with those aniline derivatives and phenol derivatives, including phenol, resorcinol, catechol, 2,6-di-*tert*-butylphenol, α-naphthol and β-naphthol. Those markers are characterized using FT-IR, ^{1}H-NMR, ^{13}C-NMR and LC-MS. In addition, the stability and properties of markers in high-speed diesel are studied.