

CHAPTER II

THEORY AND LITERATURE REVIEWS

THEORY

2.1 Color of organic compounds

Coloration of organic compounds is arisen from electronic excitation of a molecule caused by absorption of energy from irradiating white light. Only the molecules containing unsaturation or non-bonded electrons can absorb light in the visible region (400-800 nm) in such a way that some wavelengths are removed from ordinary white light, and only the remainders reach the eyes [4]. In general, the visual color is complementary to the color absorbed as indicated in Table 2-1 [5].

Table 2-1 Relation between color absorbed and visual color of a molecule.

Wavelength absorbed (nm)	Colored absorbed	Visual color
400-435	Violet	Yellow-green
435-480	Blue	Yellow
480-490	Green-blue	Orange
490-500	Blue-green	Red
500-560	Green	Purple
560-580	Yellow-green	Violet
580-595	Yellow	Blue
595-605	Orange	Green-blue
605-750	Red	Blue-green

Investigations of the correlations between chemical structure and color of organic compounds already began in the early days of dyestuff chemistry. *Graebe* and *Liebermann* found that all dyes contained a series of conjugated double bonds. In

1876, *Witt* found that two types of groups were usually presented in colored compounds, unsaturated groups, which were called “chromophore” and saturated groups that intensified the color, which were called “auxochrome”. Examples of chromophore are NO_2 , $\text{C}=\text{O}$, $\text{N}=\text{N}$, $\text{C}=\text{C}$, $\text{C}=\text{N}$, $\text{C}=\text{S}$, $\text{N}=\text{O}$ and quinonoid structure. The important auxochromes are the hydroxyl group, the amino group and the alkylated amino group. Auxochromes have lone pairs of electrons that can be delocalized along with the delocalized electrons of chromophores, which normally increase the intensity of the color and shift the absorption to longer wavelengths of light. In general, when the molecules contain extended series of conjugated multiple bonds, the absorption maximum is shifted to a longer wavelength. This effect is called “bathochromic shift” or “red shift” [5,6].

2.2 Ultraviolet-visible spectroscopy [7,8,9,10,11]

Ultraviolet-visible spectroscopy is a useful instrumental technique for characterization of the colored compounds, involves the absorption of ultraviolet-visible light (200-800 nm) by valence electrons of a molecule causing the promotion of an electron from a ground electronic state to an excited electronic state. Ultraviolet-visible radiation is absorbed by π electrons and in some cases, by unshared electron pairs on organic compounds. There are various kinds of electronic transitions that can occur in organic molecules shown in Figure 2-1.

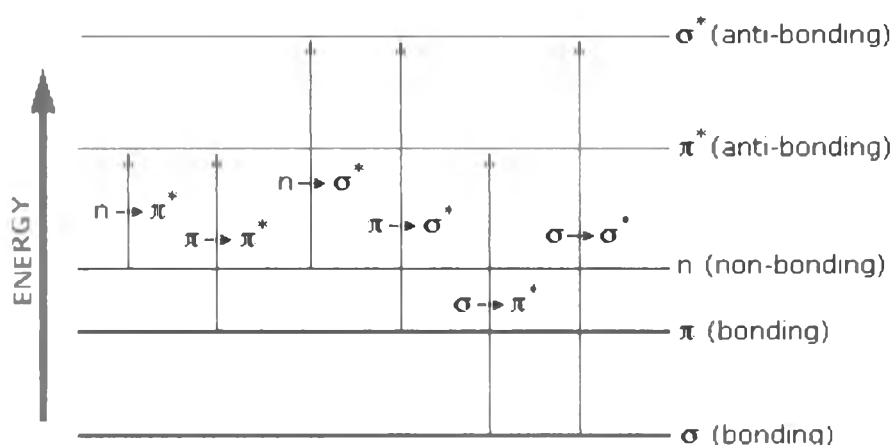
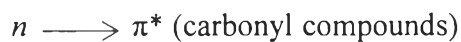
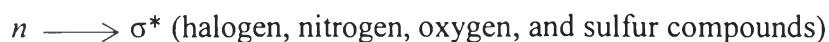
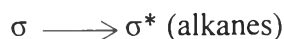


Figure 2-1 Electronic transitions of organic molecules.

Examples of organic compounds of each electronic excitations including:



As a rule, the energetically most favorable electron promotion occurs from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecule orbital (LUMO). Most electronic transitions of organic compounds involve only the transitions of n or π electrons to the π^* excited state.

In practice, an ultraviolet-visible spectrum is recorded by irradiation a sample with ultraviolet-visible light of continuously scanning the wavelength. When a wavelength corresponds to the energy level required to excite an electron to a higher level, energy is absorbed. This absorption is detected and displayed on a chart that the resulting spectrum is presented as a graph of absorbance (percent radiation absorbed) versus wavelength.

The relation between the energy absorbed in an electronic transition and the frequency (ν) and wavelength (λ) of radiation producing the transition is shown in the equation:

$$\Delta E = h\nu = hc/\lambda$$

Where ΔE = energy absorbed in an electronic transition in a molecule from a ground state to an excited state

h = Planck's constant

c = velocity of light

λ = wavelength of the absorption

The energy absorbed is dependent on the energy between the ground state and the excited state, the smaller the HOMO-LUMO gap showed the longer the wavelength of the absorption. The wavelength at which the maximum absorption band occurs in the ultraviolet-visible region is generally referred to as the λ_{max} of the sample. The λ_{max} value is the most important aspect of a spectrum when used ultraviolet-visible spectroscopy to determine chemical structure. The structure feature of a compound that is most significant in determining the λ_{max} is the number of conjugation of double or triple bonds. If a compound has enough double bonds in

conjugation, its λ_{max} value will be large enough to fall within the visible region and thereby the compound will appear colored. However, other factors are involved in determining the λ_{max} of an organic compound such as substituents.

The corrected amount of the light absorbed is known as the molar absorptivity (ϵ), formerly called the molar extinction coefficient and defined by Beer-Lambert equation:

$$\epsilon = A/cl$$

Where A = absorbance

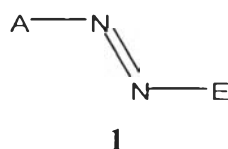
c = sample concentration (mol/l)

l = sample path length (cm)

The molar absorptivity is a physical constant, characteristic of a particular substance, which is a measure of how strongly the sample absorbs light at that wavelength. Each absorption in a spectrum has a unique molar absorptivity that depends on wavelength, solvent, and temperature. Increased conjugation brings the molar absorptivity generally becomes greater. Molar absorptivities may be very small if absorption is weak (10 to 100) and very large for strongly absorbing chromophores (>10,000).

2.3 Azo dyes [12,13]

The azo dyes are the most important chemical class of commercial dyes, accounting for around 60-70% of the dye and having been studied more than any other class. Azo dyes are compounds that contain at least one azo group ($-\text{N}=\text{N}-$) linked to aromatic sp^2 -hybridized C-atoms. Azo colorants contain a single azo group referred to as monoazo dyes, but they can contain two (disazo), three (trisazo), four (tetrakisazo) or more (polyazo) azo groups. In monoazo dyes, the azo group is attached to two groups, more usually both, are aromatic. They exist in *trans* form **1**.



The A groups often are electron-accepting substituents, and the E groups generally are electron-donating substituents, such as hydroxyl and amino groups. If the azo dyes consist of only aromatic groups, such as benzene and naphthalene, they are called “carbocyclic azo dyes”. If they consist of one or more heterocyclic groups, the dyes are called “heterocyclic azo dyes”. Examples of various commercial azo dyes are shown in Figure 2-2.

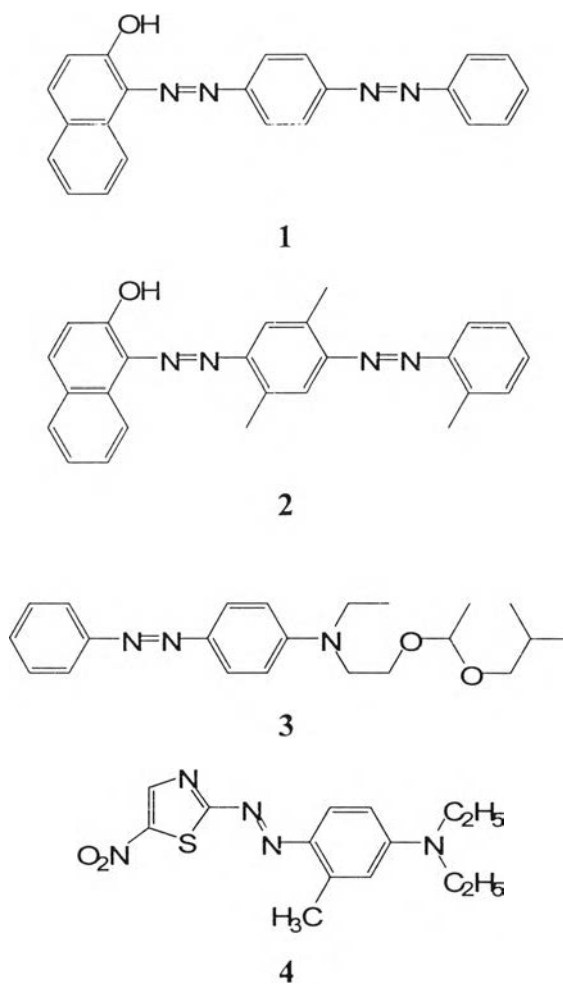


Figure 2-2 Azo dyes. *Solvent Red 164 (1)*, *Solvent Red 26 (2)*, *Solvent Yellow 124 (3)* and *C.I. Disperse Blue (4)*.

Dyes are applied as coloring agents in industrial organic solvents, and the petroleum products such as gasoline, kerosene, and diesel fuel. The coloring agent for fuels must satisfy various requirements as follow [14]:

1. To possess a high dyeing power.
2. To have a sufficient solubility in organic solvents and fuel oils, in the presence or absence of antiknock agents.
3. To have a high diffusion index.
4. To contain little or no by-product insoluble in fuels.
5. To leave only a minimum deposit of sludge in the engines.
6. To have a proper fastness to light during storage.
7. To be compatible with additives, and should not affect the other properties of the fuel.
8. To be brittle, but no powders in the solid form.
9. To be sufficiently fluid to be solubilized in organic solvents, if it is used in the form of concentrated solution.

The use in the form of concentrated solution allows many advantages, when comparing with powdery products, such as convenient to use, high diffusion coefficient, and absence of powders.

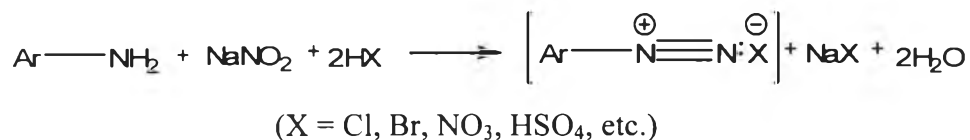
2.3.1 General synthesis [6,15,16]

Azo dyes are prepared by two-stage sequence of reactions. The diazotization of a primary aromatic amine is the first step, followed by coupling of the resultant diazonium salt with an electron-rich nucleophile. Since many diazonium ions decompose rapidly in solution, it is necessary to conduct the reaction under temperature range 0–5 °C, and use freshly prepared diazonium ions.

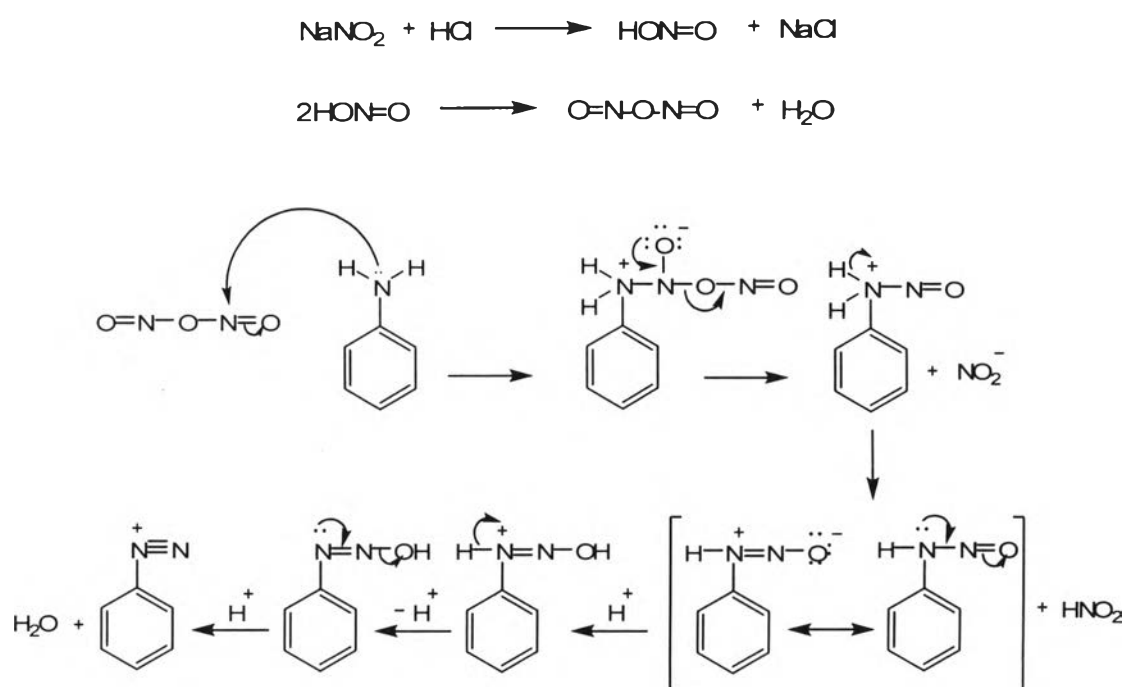
2.3.1.1 Diazotization reaction

Diazotization, the first of two reaction steps by which almost all azo dyes are produced, involves the treatment of a primary aromatic amine (ArNH_2) with nitrous acid to form a diazonium salt. Normally, an ice-cold aqueous solution of the amine is converted to a diazonium salt upon adding sodium nitrite (NaNO_2) and mineral acid such as hydrochloric acid according to the equation is shown below. Thereby, the use of at least 2 equivalence of acid is essential for a smooth reaction. The nitrous acid

nitrosates the amine to generate the *N*-nitroso compound, which tautomerises to the diazonium hydroxide. Protonation of the hydroxyl group followed by the elimination of water generates the diazonium salt. Efficient cooling is required to maintain a temperature at which the diazonium salt is stable due to higher temperature promote the decomposition of nitrous acid into oxides of nitrogen.



The mechanism of reaction may be summarized as follows:

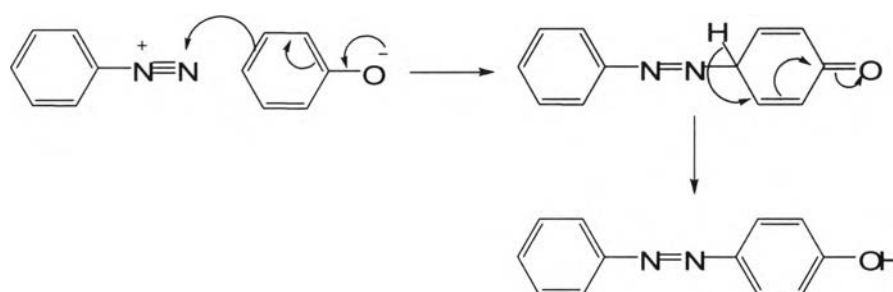


Scheme 2-1 Mechanism of diazotization.

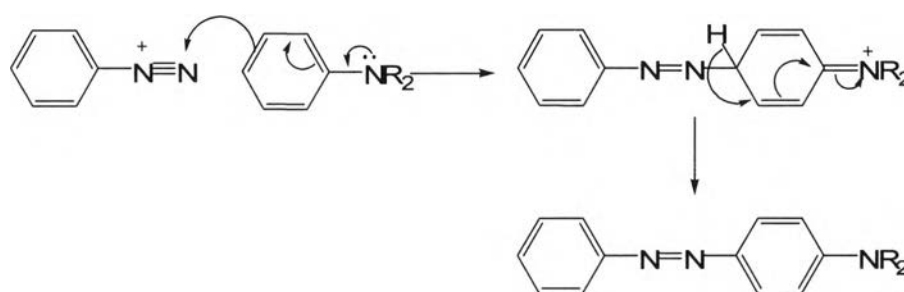
Aromatic amine, which has the electron-withdrawing groups as substituents in an aromatic ring, is less easy to diazotize, due to the nucleophilicity of the amino-nitrogen is reduced by the partial withdrawal of the unshared electron pair into the ring.

2.3.1.2 Coupling reaction

Azo coupling is an electrophilic aromatic substitution in which the electrophile is the diazonium cation. The diazonium salt is a weak electrophile and hence reacts only with highly electron rich species such as amino and hydroxyl compounds, referred to as coupling components. The coupling of diazonium ion with phenol occurs *via* the phenoxide ion. The experimental factor that requires control in coupling reaction is pH. The optimum pH for coupling with phenol is about 9 to 10, but it is common to add an acidic solution of the aqueous diazonium ions to a solution of the phenoxide ions in sufficient amounts of alkali to neutralize the acids formed, and to maintain suitable alkalinity. Coupling reaction occurs rapidly to prevent destruction of the diazonium ion. The mechanism of coupling reaction between phenoxide ions and diazotized amine is directed mainly to the *para* position, e.g.



Coupling reaction of aromatic amine and diazotized amine also occurs in the same way, e.g.



Scheme 2-2 Mechanism of coupling reaction.

The coupling reaction is an electrophilic substitution involving the diazonium ion, which react at the position of greatest electron availability, such the *ortho* or *para* position of coupling components. Generally, strongly electrophilic diazonium ions preferably attack at the *para*-position. When the *para* position is already substituted, *ortho*-coupling occurs, but coupling reaction is never reacted at the *meta* position.

2.4 Gasoline fuel [17,18,19]

Gasoline is a complex liquid mixture of hydrocarbons of four basic types: paraffins, olefins, naphthalenes, and aromatics, differing in their properties according to the number of carbon and hydrogen atoms in the molecule. Gasoline, having a boiling range of 32–204 °C (90–400 °F) is derived from crude petroleum by refining and contains 6–10 carbon atoms in each molecule. Gasoline is more volatile than diesel oil, Jet-A or kerosene, not only because of the base constituents, but because of the additives that are put into it. An important characteristic of gasoline is its octane rating, which is a measure of how resistant gasoline is to the abnormal combustion phenomenon known as knocking. Gasoline has two types namely:

1. Regular motor gasoline (octane number 91), which its color is red.
2. Premium motor gasoline (octane number 95), which its color is yellow.

2.4.1 Chemical composition [20]

Gasoline is a product that refined from petroleum, consist of a mixture of hydrocarbons, additives, and blending agents. The composition of gasolines depends on the crude oils used, the refinery processes available, the overall balance of product demand, and the product specifications. The typical composition of gasoline hydrocarbons (% volume) is as follows: 4–8% alkanes; 2–5% alkenes, 25–40% isoalkanes; 3–7% cycloalkanes; 1–4% cycloalkenes and 20–50% aromatics. To improve the performance and stability of gasoline, additives and blending agents are added to the hydrocarbon mixture. These compounds are anti-knock agents, anti-oxidants, metal deactivators, lead scavengers, anti-rust agents, anti-icing agents, upper-cylinder lubricants, detergents, and dyes. ASTM specifications for gasoline 91 are summarized in Table 2-2 [21].

Table 2-2 ASTM specifications for gasoline 91.

Test Items	ASTM method	Limit	Unit
Research Octane Number; RON	D 2699	Min 87	
Lead content	D 5059	Max 0.013	g/L
Sulfur content	D 4294	Max 0.05	%wt.
Phosphorus content	D 3231	Max 0.0013	g/L
Silver strip corrosion	D 4814	Max No.1	
Solvent Washed Gum	D 381	Max 4	mg/100 mL
Distillation : Initial Boiling Point (IBP)	D 86	Report	°C
Distillation : 10% Evaporated	D 86	Max 70	°C
Distillation : 50% Evaporated	D 86	Min 90 and Max 110	°C
Distillation : 90% Evaporated	D 86	Max 170	°C
Distillation : Final Boiling Point (FBP)	D 86	Max 200	°C
Distillation : Residue	D 86	Max 2.0	%vol.
Vapor pressure @ 37.8 °C	D 4953	Max 54.5	kPa
Benzene	D 5580	Max 3.8	%vol.
Aromatics	D 5580	Max 38	%vol.
Olefins	D 1319	Max 20	%vol.
Water content	E 203	Max 0.7	%wt.
Oxidation Stability	D 525	Min 360	minutes

2.5 Cashew Nut Shell Liquid (CNSL) [22,23]

Cashew nut shell liquid (CNSL) is the international name of the alkylphenolic oil that occurs as a reddish brown viscous liquid obtained from the spongy layer between the inner and the outer shell of the cashew nut (*Anacardium occidentale* L.). CNSL is an agricultural renewable resource and the undesirable by-product obtained from cashew kernel industry. Since worldwide cashew nut production is presently estimated to be 1,200,000 tons per annum, the availability of CNSL ranges between 300,000–360,000 tons per annum. Nowadays, CNSL becomes a valuable raw material in the manufacture of commercial important products for various industries.

2.5.1 Extracting process of CNSL [24, 25]

Traditionally, CNSL is an oil obtained during thermal processes of deshelling the cashew nuts for the purpose of obtaining the edible part, the cashew kernels.

There are two processes to obtain cashew nut shell liquid from cashew nut:

1. Hot oil bath method.

The “hot oil bath” method is the most common commercial method of extracting CNSL. The raw humidified cashew nuts are passed through a hot bath of CNSL (180–190°C) for about 90 s. The heat causes the outer part of the shell burst open and releases CNSL (50% recovery). Another 20% could be extracted by passing the spent shells through an expeller and the rest by solvent extraction techniques.

2. Low temperature solvent extraction.

In the low temperature solvent extraction process, intact shells were cooled at low temperature to solidify the phenols before the manual disintegration, followed by the solvent extraction on the separated shell.

CNSL, extracted with low boiling petroleum ether, contains about 90% anacardic acid and about 10% cardol. On distillation, CNSL gives the pale yellow phenolic derivative cardanol.

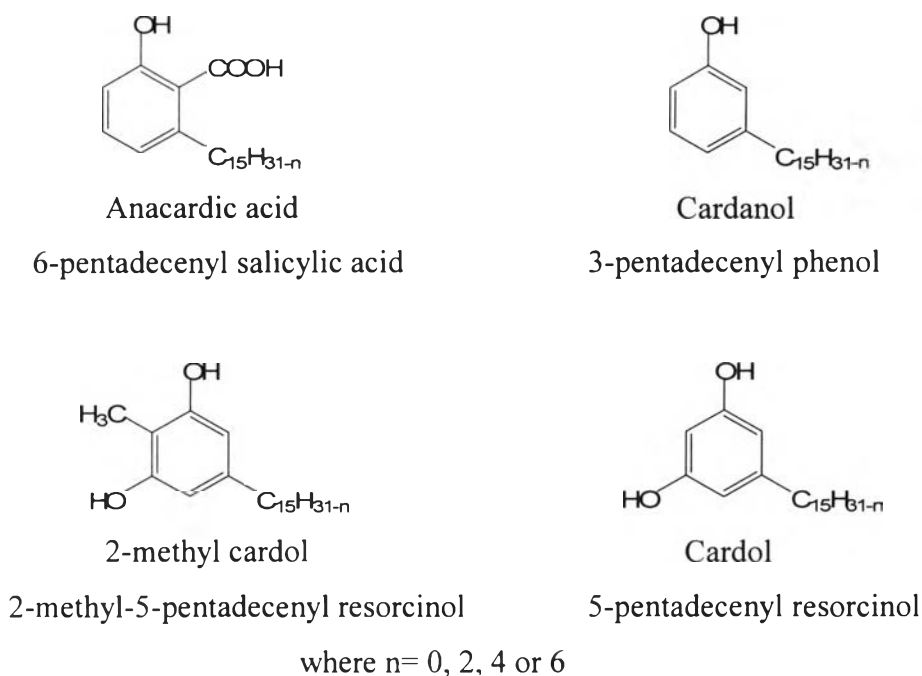


Figure 2-3 Chemical structure of components in natural CNSL.

CNSL is essentially a mixture of phenolics extracted from the shells of the cashew nut and contains four components namely, 3-pentadecenyl phenol (cardanol), 5-pentadecenyl resorcinol (cardol), 6-pentadecenyl salicylic acid (anacardic acid) and 2-methyl-5-pentadecenyl resorcinol (2-methyl cardol). The chemical structures of components in natural CNSL are shown in Figure 2-3. The side chain exists in saturated ($n=0$), monoene ($n=2$), diene ($n=4$), and triene ($n=6$) that form with *cis* configuration. The major component of CNSL, depending slightly on the geographical location of the tree, is anacardic acid, which has yield up to 70–80% and purity up to 90%. It is easily thermal decarboxylated and breaks down to give cardanol, which is much stable phenol than anacardic acid.

Cardanol is a mono hydroxyl phenol with a C_{15} aliphatic chain substituted in the meta position, obtained from cashew nut shell liquid (CNSL) as a mixture of saturated and unsaturated compounds and has an average of 1.7 double bonds per molecule. The structure and composition of cardanol is given in Figure 2-4 [26]. The physical and chemical properties of cardanol are shown in Table 2-3 [27].

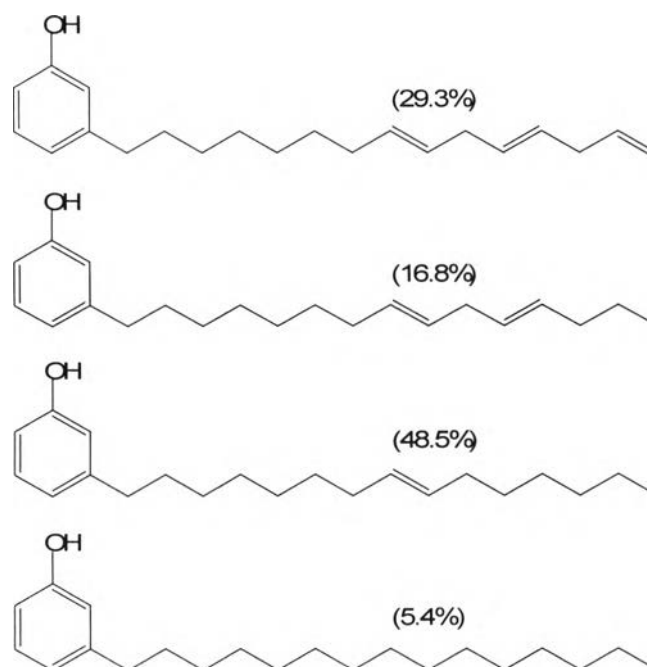


Figure 2-4 Structure and composition of cardanol.

Table 2-3 Characteristics of cardanol.

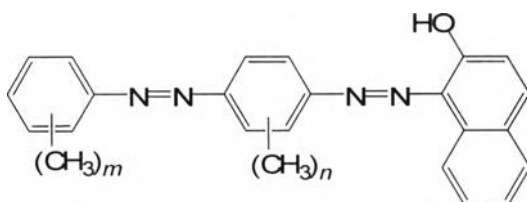
Boiling point, °C	228–235 (3.4 mmHg)
Color (Livibond, 1 cm cell) (freshly distilled)	Red (1.0–3.0) Yellow (1.5–3.5)
Viscosity, 30°C (cP)	40–60
Specific gravity 30/30 °C	0.93–0.95
Volatile loss, % by wt (max)	2.0
Acid value	1.9–2.0
Iodine value (Wijs method)	210–220
Hydroxyl value	180–200

2.5.2 Uses and applications

CNSL is used commercially as a cheap phenolic raw material for the manufacture or modification of phenolic resin for using as fillers [28]. In particular, it is used as a friction modifier in the manufacture of brake linings and clutch facings. It has the property of absorbing the heat generated by friction in the braking action while retaining their braking efficiency longer [29]. It is also used in rubber compounds, where it acts as vulcanizing agents by mixing with natural rubber and other additives. The mechanical properties of the resulting rubber, such as tensile strength, hardness, elongation and rebound resilience, are improved [30]. CNSL is used as dispersants and plasticizers for natural rubber and alumina tape casting slips [26]. Furthermore, hydrogenated cardanol represented a simple and easily available entry to various derivatives useful for different purposes such as antioxidants, flame-retardants, water-proofing agents and gum inhibitors for gasoline [23,31]. Other applications include the manufacture of lacquers, paints, printing inks, electrical insulation material, impregnating materials, anti-corrosive for metals, laminates, insulating varnishes, surface coating, adhesives, insecticides and fungicides [32,33,34].

LITERATURE REVIEWS

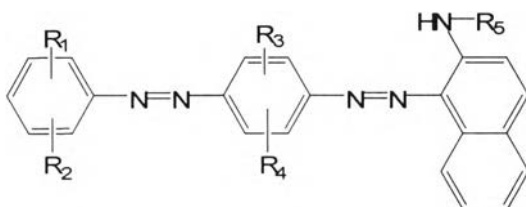
Kesler *et al.* reported the synthesis of the oil soluble red dye for coloring petroleum products [35]. Oil soluble dye composition comprising a mixture of compounds having the general formula:



where the m and n are each 1 or 2.

These compounds were synthesized by diazotizing of a mixture of aminoazotoluenes and aminoazoxylenes, which are the products from coupling reaction of diazonium salts of a toluidines/xylidines mixture and another toluidines/xylidines mixture. Subsequent coupling of the resulting mixture with excess β -naphthol in an alkaline solution led to red disazo dyes. These compounds are used as colorants for petroleum products such as gasoline and fuel oils, which is free of dust, readily soluble in hydrocarbons and resistance to caking at temperatures from ambient to 65°C.

Orelup synthesized azo dyes which are highly soluble in petroleum fuels having the following structure [1]:

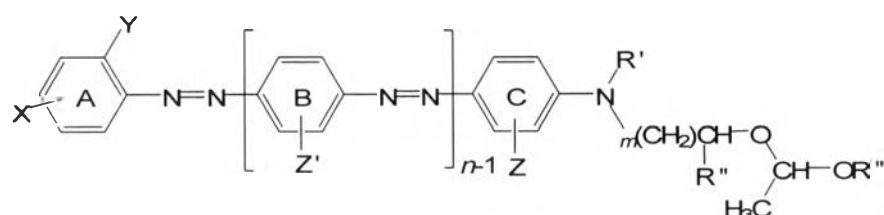


where the R_1 , R_2 , R_3 , and R_4 are each H or CH_3 and R_5 is either 2-ethylhexyl or 2-ethylhexyloxypropyl.

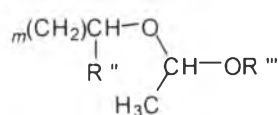
These compounds were conveniently synthesized by coupling reaction of diazonium salt of aminoazotoluene with 2-ethylhexylamino naphthalene or coupling reaction of diazonium salt of aminoazobenzene with 2-ethylhexyloxypropylamino

naphthalene. These azo dyes are used for coloring petroleum products. They are non-solids at room temperature and highly soluble in petroleum fuels. Moreover, they do not affect the physical or chemical properties of the petroleum fuels such as gasoline, diesel oils, heating oils, kerosenes and jet fuels. The color of these azo dyes are blue red or yellow-red.

De Feo *et al.* synthesized azo dyes which are highly soluble in organic solvents for coloring petroleum products [36]. The general formula is shown below:



where m is 1 to 3; n is 1 or 2; X is H or NO_2 ; Y is H, Cl, NO_2 , lower alkyl or lower alkoxy radicals containing from 1 to 3 carbon atoms; Z and Z' are H, Cl, lower alkyl or alkoxy radicals containing 1 to 3 carbon atoms, or lower acylamine groups; R' is alkyl or

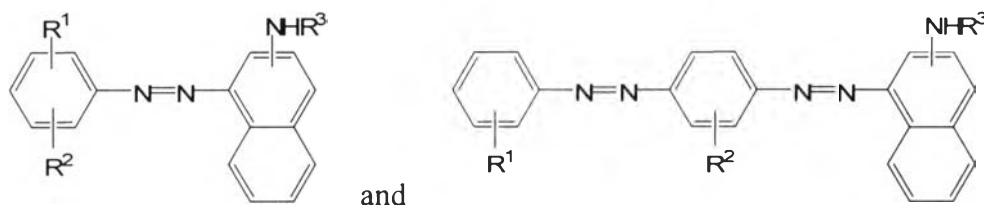


; R'' is H, or a lower alkyl radical containing 1 to 3

carbon atoms; and R''' is an alkyl radical containing from 1 to 18 carbon atoms, or a cycloalkyl radical. The aromatic nuclei A, B and C may have other water-insoluble substituents.

These compounds were synthesized by coupling reaction of diazonium salt of aminoazobenzene having water-insoluble substituents with aniline having water-insoluble substituents. The medium for this reaction was anhydrous inert organic solvents include toluene, xylene and chlorobenzene. The advantage derives from varying the substituents R' , R'' , R''' , X , Y and Z in the formula, to obtain shades from yellow to violet. Compounds of this general formula are adapted to use as coloring agents for a wide variety of materials including inks, synthetic plastics, wood, oils and natural and synthetic waxes. Especially, these azo dyes are eminently suitable for use in coloring gasoline, gas oil, lubricating oils and similar liquid petroleum distillates. The azo dyes obtained from this invention are high coloring power and solubility in organic solvents, and are stable to recrystallization at low temperatures.

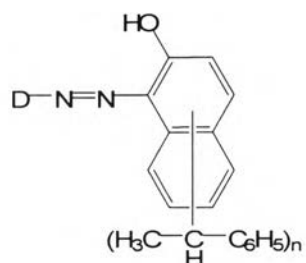
Zeidler *et al.* reported the synthesis of monoazo and disazo dyes which are soluble in oil and have N-substituted β -naphthylamine as coupling component [37]. The general formula is shown as follows:



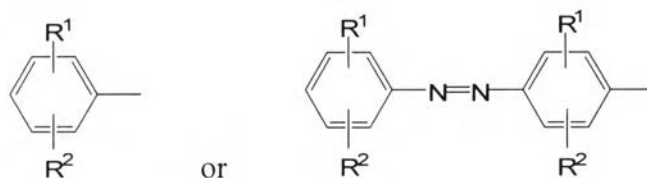
where R^1 and R^2 are H, C_1 - C_4 alkyl group, methoxy or ethoxy and R^3 is C_6 - C_{13} alkyl group, alkoxypropyl of four to eight carbon atoms in the alkoxy, cyclohexyl, benzyl or phenylethyl and in which the NHR^3 group is in the *o*- or *p*-position to the azo bridge.

These monoazo and disazo dyes have an unsubstituted or substituted aniline or *p*-aminoazobenzene as diazo component and an N-substituted β -naphthylamine of six to eighteen carbon atoms in the N-substituent as coupling component. These compounds were prepared by coupling reaction of diazonium salt of unsubstituted or substituted aniline or diazonium salt of *p*-aminoazobenzene with N-substituents β -naphthylamine. These resulting dyes are normally red oils, waxy substances or powders. They have good solubility in aromatic, aliphatic and also chlorinated hydrocarbons, esters and alcohols, and therefore suitable for using as coloring agents in fuels, fuel oils, surface coatings, waxes and fats. These ready-to-use dye solutions can be produced without isolating the pure dye. The concentrated solutions of dye in hydrocarbons such as toluene, xylene, high-boiling mixtures of aromatic hydrocarbons, gasoline and paraffin oils are particularly valuable as colorants in the range from 20 to 70% by weight in industry.

Hansen described the synthesis of monoazo and disazo dyes for dyeing petroleum products, waxes and greases, soluble in organic solvents [38]. The general structure is shown as follows:



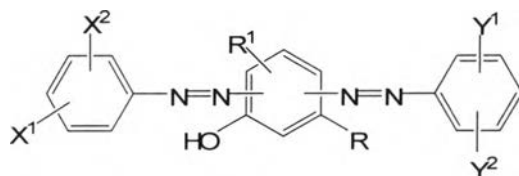
where D is a radical of the formula



where n is 0, 1, 2 or 3 and R^1 and R^2 independently of one another are hydrogen, C_1 - C_4 alkyl, methoxy or ethoxy.

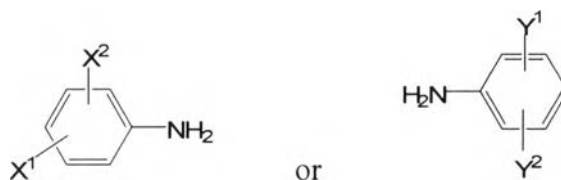
These azo compounds were prepared by coupling reaction of diazonium compound of substituted amine or aminoazobenzene mixtures with coupling component which obtained by reacting β -naphthol with styrene using an acid catalyst. The mixtures of these compounds of this general formula are distinguished by excellent solubility in organic solvents, especially hydrocarbons such as benzene, toluene, xylene and ethylbenzene. Because of their solubility, these orange or red azo dyes are exceptionally suitable for dyeing motor fuels, fuel oils, surface coatings, waxes and greases.

Armbrust *et al.* reported the synthesis of disazo dyes for coloring petroleum products, solvents and engine fuel additives with the following general formula [39]:

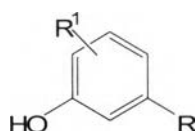


where R is hydroxyl or unsubstituted or substituted amino; R¹ is hydrogen or C₁-C₁₂ alkyl; X₁ and Y₁ are each a carboxylic acid ester or ether group and X₂ and Y₂ are each hydrogen, nitro or chlorine.

These compounds were synthesized by reacting diazonium compounds of amines of the formula:



with a coupling component of the formula:



The disazo dyes are from yellow to red, depending on varying the substituents. They are particularly useful for coloring petroleum products, solvents and gasoline additives since they are highly soluble in these liquids.

Pansare, V.S. *et al.* reported the synthesis of monoazo and disazo dyes from coupling reaction of the diazonium salts of various aromatic amines with 3-pentadecylphenol (hydrogenated cardanol) [2]. Following a procedure, one mole of each aniline derivatives, such as *p*-chloroaniline, *o*-anisidine, *p*-anisidine, *o*-nitroaniline, *m*-nitroaniline, *p*-nitroaniline, anthranilic acid, α -naphthylamine, β -naphthylamine, 2,5-dichloroaniline and *p*-toluidine, was diazotized and coupled with one mole of 3-pentadecylphenol, resulting in the corresponding monoazo and disazo dyes. In case of benzidine, one mole of benzidine was required to form disazo dyes.

The synthesis of these azo dyes used cardanol as the starting material, which has a long alkyl side chain, providing a great advantage for improving properties such as solubility in oil, penetration in leather and water-repellance.

Suwanprasop, S. *et al.* synthesized petroleum marker dyes from cardanol and aniline derivatives [3]. The general formula is shown as follows:



where $n = 0, 2, 4, 6$; R_1 is H, NO_2 , Cl, CH_3 or OCH_3 ; R_2 and R_3 are H, NO_2 , Cl or CH_3 and R_4 is H or NO_2 .

These monoazo dyes were prepared by coupling reaction of the diazonium salt of an aniline derivative with non-hydrogenated cardanol. Aniline derivatives in this study include aniline, 4-nitroaniline, 3-nitroaniline, 2-nitroaniline, 4-chloroaniline, 3-chloroaniline, 2-chloroaniline, 2-chloro-4-nitroaniline, 2-chloro-5-nitroaniline, 4-chloro-2-nitroaniline, 4-chloro-3-nitroaniline, 4-methylaniline, 3-methylaniline, 2-methylaniline and 2-methoxy-4-nitroaniline. The synthetic compounds showed potential to be applied as marker for the commercial fuel oil such as gasoline and high-speed diesel fuel. These markers provided invisible color in gasoline and diesel fuel at 2–5 ppm, but gave visible color when extracted by 50% v/v 1,2-diaminoethane in a 1:1 v/v solution of ethane-1,2-diol:methanol. The marker dyes did not exhibit significant effects on the physical properties of fuel oil and were found to be stable in fuel oil for at least three months.