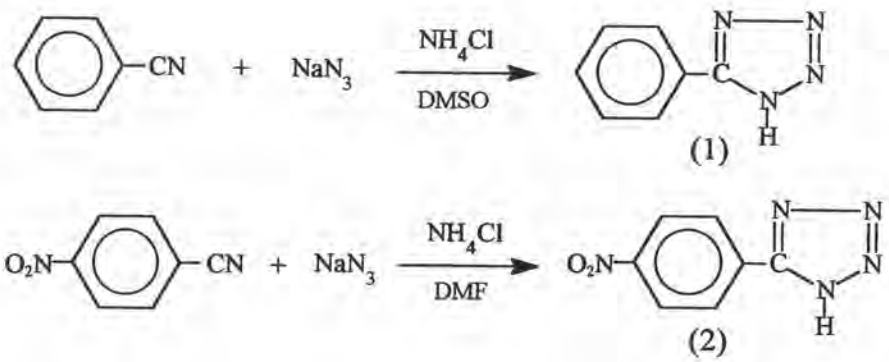
CHAPTER IV

RESULTS AND DISCUSSION

Synthesis of tetrazole derivatives

In this thesis, there were many approaches for the tetrazole derivatives. Tetrazole derivatives were synthesized as follows.

1. Tetrazole derivatives can be prepared by direct synthesis from sodium azide and arylnitrile derivatives. It was refluxed at 115-120 °C, 24 hours for synthesis of 5-phenyltetrazole(**1**) and 100-104 °C, 5 hours for synthesis of 5-(4′-nitrophenyl)tetrazole(**2**). The addition of 10 % by mole of ammonium chloride to react with sodium azide raised the yield of tetrazole derivatives. This synthesis of tetrazole derivatives are indicated in the following reaction:



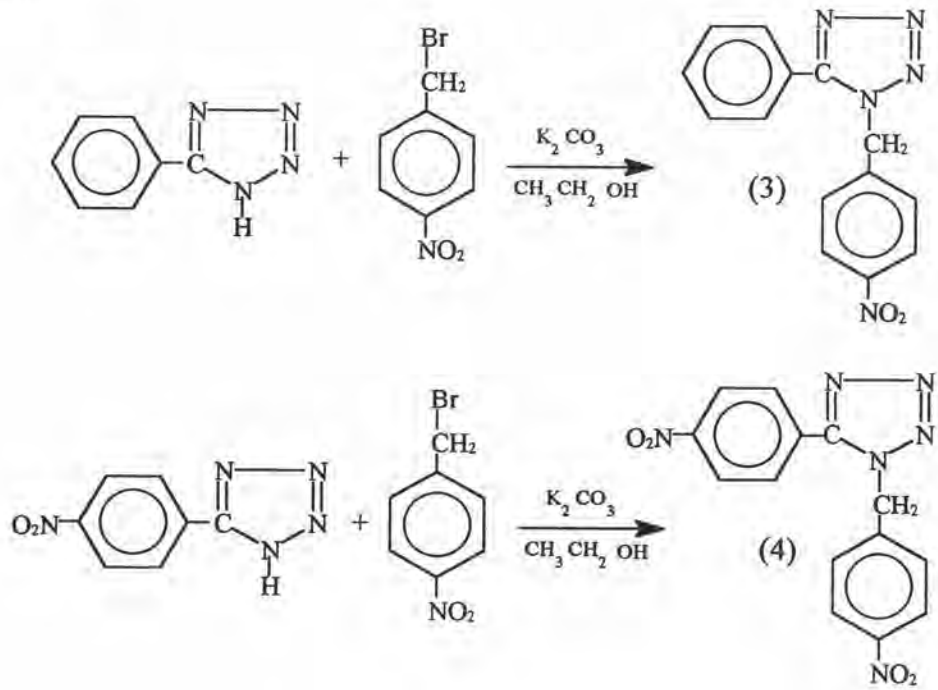
Scheme 4.1

5-phenyltetrazole(**1**) and 5-(4′-nitrophenyl)tetrazole(**2**) were synthesized using this method with quantitative yields of 84 % and 57 %, respectively.

2. Tetrazole derivatives can be prepared by nitroarylation of the 5-substituted tetrazole compound such as 5-Phenyltetrazole **(1)** and 5-(4′-nitrophenyl)tetrazole **(2)**. **(1)** or **(2)** was treated with p-nitrobenzyl bromide in aqueous ethanol solution.

This method can be used to synthesize tetrazole derivatives such as 1-(4″-nitrobenzyl)-5-phenyltetrazole**(3)**, 1-(4″-nitrobenzyl)-5-(4′-nitrophenyl) tetrazole **(4)**. The reaction was refluxed for 4 hours and at 75-80 °C. In this study the result product **(3), (4)** were 87, 78 %yield base on 5-phenyltetrazole, respectively.

This synthesis of tetrazole derivatives are indicated in the following reaction:



Scheme 4.2

The characteristics of tetrazole derivatives were monitored by FTIR spectrum, ^{1}H-NMR spectrum, ^{13}C-NMR spectrum, mass spectrum as shown in appendix A.

To determine the cetane number improver properties, tetrazole derivatives were dissolved in alcohol and blended in base diesel fuel. The test was carried out according to ASTM methods.

Tetrazole derivatives on the physical properties in base diesel fuel

1. Some physical properties of alcohols and in base diesel fuel

In this study, the alcohols such as ethanol, 2-butanol, 1-hexanol and 1-octanol was used and tested the physical properties of these alcohols and in base diesel fuel as presented in table 4.1.

Table 4.1 Some physical properties of alcohols and in base diesel fuel

Properties	Ethanol	2-Butanol	1-Hexanol	1-Octanol
Mid-boiling point[1] (°F)	176.0	212.0	312.8	381.2
API gravity[2] at 40 °C	47.6	43.8	41.4	40.2
Cetane index[3]	- 41.4	- 26.3	13.9	32.2
Solubility in diesel fuel	non soluble	soluble	soluble	soluble
Solubility of Tetrazole derivatives	soluble	soluble	soluble	partial-soluble
Flash point[4], (°C)				
2.5 %v/v in diesel fuel	-	48	66	73
5.0 %v/v in diesel fuel	-	43	63	73

Note: [1] ASTM D86 [2] ASTM D1298
[3] ASTM D976 [4] ASTM D93

From the table 4.1, the 1-hexanol was used as solvent in this study due to the limitation of Flash point (minimum 52 °C), solubility property and effect on cetane index as compare to the other alcohols.

2. The effect of % by volume of 1-hexanol on cetane index and some properties in base diesel fuel

In this study, the data were taken from the sample contains of 0, 2.5, 5.0, 7.5, 10.0, 15.0 % by volume of 1-hexanol which was the acceptable range of practical blends in base diesel fuel. The results from cetane index determinations of diesel composition base mixed with 1-hexanol were presented in table 4.2.

Table 4.2 The effect of 1-hexanol on cetane index and some properties

%V 1-hexanol in base diesel fuel	Mid-boiling point, (°F)	API gravity @ 60 °F	Flash point, (°C)	CCI
0.0	518.0	35.5	73	48.75
2.5	514.4	35.7	66	48.67
5.0	512.6	35.8	63	48.62
7.5	507.2	35.9	62	48.13
10.0	505.4	36.0	61	48.08
15.0	500.0	36.3	61	47.89

Note : diesel base fuel was composed of %Cp, %Cn, %Ca such as 26.78, 69.79, 3.43, respectively as shown in appendix C.

CCI = calculated cetane index

From table 4.2, it can be seem that 1-hexanol had no significantly effect on cetane index. It only has a little effect on mid-boiling point and flash point. Then 1-hexanol can not be used more than 5 % by volume in base diesel fuel.

This thesis, it was not studied the effect of 1-hexanol on cetane number because of the cost per sample was exppensiveness.

3. Determination of cetane index of 1-hexanol and tetrazole derivatives in diesel base fuel

Tetrazole derivatives as 0.05 % by weight were dissolved in 2.5 % by volume of 1-hexanol base on diesel fuel. The cetane determination was made by Petroleum Authority of Thailand (PTT). The cetane index of their blend compositions were determined and presented in table 4.3.

Table 4.3 Cetane index of the blend of tetrazole derivatives and 1-hexanol with base diesel fuel

Blend composition	Mid-boiling point, (°F)	API gravity @ 60 °F	CCI	Improver value	CCI improver
base + a	514.4	35.7	48.67	-	48.67
base + a + A	514.0	35.7	48.63	3.58	52.21
base + a + B	513.8	35.7	48.60	3.57	52.17
base + a + C	513.3	35.7	48.54	3.57	52.11
base + a + D	514.2	35.7	48.65	3.58	52.23

Note : a = 2.5 % by volume of 1-hexanol

A = 5-phenyltetrazole

B = 5-(4′-nitrophenyl)tetrazole

C = 1-(4″-nitrobenzyl)-5-phenyltetrazole

D = 1-(4″-nitrobenzyl)-5-(4′-nitrophenyl)tetrazole

CCI improver = CCI + Improver value

CCI = Calculated cetane index

From table 4.3, it can be seen that CCI improver had no significantly effect on tetrazole derivatives content. Because of their compositions were calculated by similar improver value equation. Thus, cetane index was not differential value. But cetane index of their blends was increased 1-hexanol when increased of tetrazole derivatives content in base diesel fuel. The cetane index was increased by abount 3 units.

Cetane index was not exacting value because of the limitations of calculated cetane index as follows: [ASTM D976]

1. It was not applicable to fuels containing additives for raising cetane number.

2. It was not applicable to pure hydrocarbons, synthetic fuels, alkylates or coal tar and products. The improver value can be calculated by its follow equation: [12]

$$\text{Improver value} = 0.1742(0.1G)^{1.4444}\,(0.1M)^{1.0052}\,\{\ln(1+17.5534D)\}$$

where

G = API gravity, determined by Test Method D287 or D 1298,

M = mid-boiling temperature, °F, determined by Test Method D86

D = percent weight of cetane improver, % wt.

4. Determination of cetane index and cetane number of mixture of 1-hexanol and tetrazole derivatives comparison with octylnitrate in base diesel fuel

The cetane index and cetane number of various diesel composition bases blended with 2.5 % by volume of 1-hexanol and tetrazole derivatives or octylnitrate centent 0.05 % by weight. The standard method for determining the cetane number of a diesel fuel was follwed ASTM D613 CFR engine technique. The method used a single-cylinder CFR engine, operated under the basic conditions given in table 4.4

Table 4.4 CFR engine operating conditions

Operating requirement	ASTM D613
Compression ratio	Variable 7:1 to 28:1
ignition delay (crank angle degrees)	Fixed 13°
Start of injection (crank angle degrees)	13° BTDC
Start of combustion	TDC
Intake air volume	Constant
Intake air temperature, (°C)	65 ± 1
Engine speed, (rpm)	900 ± 9
Fuel flow, (ml/min)	13 ± 0.2
Engine load, (Nm)	Not specified
Water jacket temperature, (°C)	100 ± 2
Oil temperature, (°C)	57 ± 8
Recommened reference fuels	
Primary	n-cetane/heptamethyl nonane
Secondary	Phillips Petroleum T and U Fuels

The cetane index and cetnae number of base diesel fuel blended with the mixture of 1-hexanol and tetrazole derivatives comparison with octylnitrate were presented in table 4.5.

Table 4.5 Composition and properties of blend composition in base diesel fuel

Composition	Mid-boiling point, (°F)	API gravity	Cetane index	Improver value	CCI improver	Cetane number
Base+a	514.4	35.7	48.67	-	48.67	47.8
Base+A + a	514.0	35.7	48.63	3.58	52.21	47.9
Base+B + a	513.8	35.7	48.60	3.57	52.17	48.0
Base+E + a	513.5	35.7	48.56	3.57	52.13	49.7

Note : a = 2.5 % volume of 1-hexanol

A = 5-phenyltetrazole

B = 5-(4′-nitrophenyl)tetrazole

E = octyl nitrate

From table 4.5, it could be depicted that the cetane number of the blends was increased as tetrazole derivatives or octylnitrate content increased. But cetane number of octylnitrate in base diesel fuel was increased by 1.9 units. While the diesel composition containing tetrazole derivatives were increased cetane number by 0.1-0.2 unit which were compared with diesel composition base.

From data, it showed that the diesel composition containing octylnitrate had higher cetane number than diesel composition containing tetrazole derivatives by 1.7 units.

The base diesel fuel had the effect on cetane number which was depended on composition of base diesel fuel such as %Cp, %Cn and %Ca.

Base Diesel fuel had %Cp more than other base diesel fuel. The cetane number of a base diesel fuel was due to its hydrocarbon composition. The paraffinic hydrocarbons had the highest cetane number, having a very short ignition delay period. The aromatic hydrocarbons gave low cetane values having long ignition delays, while the naphthenic hydrocarbons were between the other two types. Thus, base diesel fuel had higher % Cp which gave higher cetane number.

From table 4.5, it could be seen that CCI improver had no significantly effect on tetrazole derivatives or octylnitrate content in diesel base fuel. But cetane index was increased by 3.5 units which were compared with base diesel fuel. The difference between the cetane index, and cetane number, was generally 1 to 2 units for base diesel fuel. [13]

From the results, the tetrazole derivatives **(3)** and **(4)** were not using for test cetane number. Because theirs structure had increased aromatics content which had poor ignition quality and expected that they will have a little effect on increasing a cetane number.

The cetane number was determined and presented in table 4.5, aryltetrazole or nitroaryltetrazole derivatives were not suitable for using as cetane improver, because the main structure formula of aryltetrazole or nitroaryltetrazole derivatives was benzene ring which had very poor ignition performance. Thus, aryltetrazole and nitroaryltetrazole derivatives do not enhance ignition quality.