CHAPTER III

EXPERIMENTAL

Apparatus and Chemicals

1. Apparatus

1. Fourier-Transform NMR Spectrometer
   model AC-F 200 (200 MHz), Bruker Spectrospin
2. Gas Chromatograph-Mass Spectrometer
   model VG Trio-2000, Fisons Instruments
3. Fourier-Transform Infrared Spectrophotometer
   model 1706, Perkin Elmer
4. Pensky-Martens Closed Flash tester
   model ISL PMFP-93, Perzoo
5. Viscometer
   model K-234 A, Hochler Instrument Co., Inc.
6. Pour point Tester
   model A82, HAAKE
7. Sulfur Analyzer
   model SLFA-800; HOBIRA
8. Colorimeter
   The Fisher ASTM colorimeter
9. Apparatus for reflux
   A round-bottomed flask was equipped with a claisen connecting tube, a water-cooled condenser and a gas trap.
10. ASTM-CFR engine
    model Wis 53186, Waukesha Motor Co., Inc.

2. Chemicals

Reagents and raw materials were obtained from various suppliers as shown in Table 3.1.

Table 3.1 Source of chemicals

Materials	Company
Acetone, reagent grade	Baker
Ammonium chloride, reagent grade	Fluka
2-Butanol, reagent grade	Fluka
Chloroform, reagent grade	Carlo Erba
Dimethylformamide, reagent grade	Carlo Erba
Dimethylsulfoxide, reagent grade	Merck
Ethanol absolute, reagent grade	Carlo Erba
1-Hexanol, reagent grade	Fluka
Methanol, reagent grade	Baker
Hydrochloric acid, reagent grade	Baker
4-Nitrobenzylbromide, reagent grade	Merck
Potassium carbonate, reagent grade	Fluka
4-Nitrobenzonitrile, reagent grade	Fluka
Benzonitrile, reagent grade	BDH
1-Octanol, reagent grade	Fluka
Sodium azide, reagent grade	Merck
Diesel base fuel	Oil Refinery

Experimental Procedure

Preparation of Tetrazole Derivatives

1. Preparation of 5-Phenyltetrazole (1)

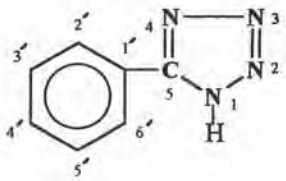
A mixture of benzonitrile (15.0 ml, 0.145 mol), sodium azide (9.76 g, 0.150 mol), ammonium chloride (0.8030 g, 1.50×10^{-2} mol) and dimethylsulfoxide 100 ml was heated to reflux at 115-120 °C for 24 hours with stirring. The mixture was cooled to room tenperature and acidified with concentrated hydrochloric acid to pH 2. The mixture was cooled to 5 °C in an ice-bath. The product (1) was removed by filtration, washed with several portions of ice-water and dried. The yield of 1 was 17.75 g (84%) , white solid, m.p. 214-215 °C, (literature[17] mp. 213-215 °C) and spectroscopic data of 1 as shown in page 40-42.

Spectroscopic data of 1

IR ν_{max} (KBr disc)

Wave number (cm^{-1})	Bond type
3130	N-H stretching
3050	C-H stretching, aromatic
2980 , 2830	C-H stretching, aliphatic
1610 , 1480 , 1460	C=C stretching, aromatic
1565	C=N stretching
1410 , 1380	C-H bending, aliphatic
1280	C-N stretching
1250	N-N=N stretching
1080 , 1035	characteristic band of tetrazole ring
720 , 700	C-H bending , aromatic

^{1}H-NMR (dimethyl sulfoxide-d_6)

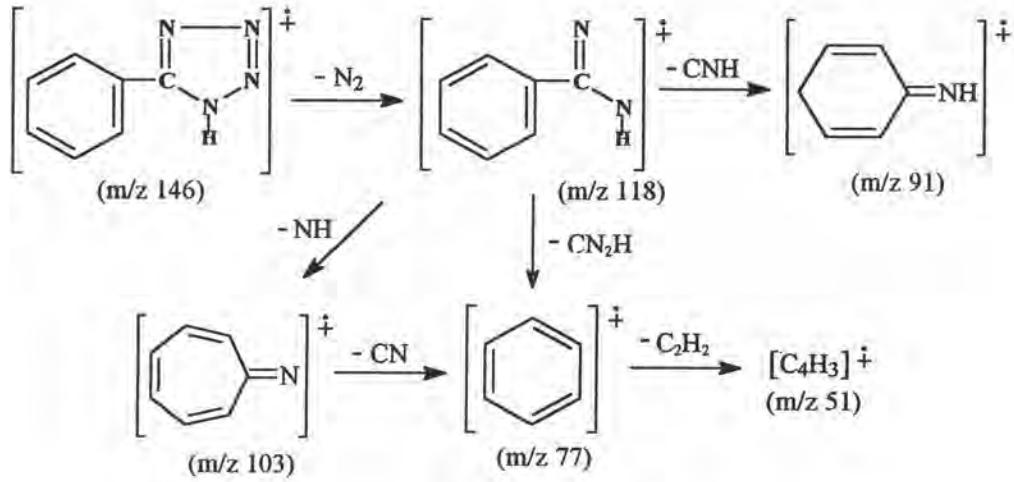


Chemical shift (δ, ppm)	Multiplicity	Position of proton	Number of proton
7.60	m	2′, 4′, 6′	3
8.05	m	3′, 5′	2
3.80	broad	1	1

^{13}C-NMR (dimethyl sulfoxide-d_6)

Chemical shift (δ, ppm)	Carbon type	Position of carbon
124.0	C	1′
126.9	CH	3′, 5′
129.4	CH	2′, 6′
131.3	CH	4′
155.3	C	5

Mass Spectrum of 1 (MW 146) see in appendix A



2. Preparation of 5-(4′-Nitrophenyl)tetrazole (2)

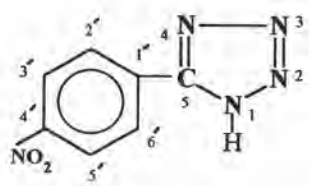
A mixture of 4-nitrobenzonitrile (5.18 g, 3.50×10^{-2} mol), sodium azide (2.93 g, 4.51×10^{-2} mol), ammonium chloride (0.242 g, 4.52×10^{-3} mol) and dimethylformamide 100 ml was heated to reflux at 100-104 °C for 5 hours with stirring. The mixture was cooled to room tenperature and acidified with concentrated hydrochloric acid to pH 2. The mixture was cooled to 5 °C in an ice-bath. The product (2) was removed by filtration, washed with several portions of ice-water and dried. The yield of 2 was 3.81 g (57%), yellow solid, m.p. 171-172 °C, and spectroscopic data of 2 as shown in page 43-44.

Spectroscopic data of 2

IR ν_{max} (KBr disc)

Wave number (cm^{-1})	Bond type
3210	N-H stretching
3090	C-H stretching, aromatic
2910 , 2850	C-H stretching, aliphatic
1610 , 1510 , 1440	C=C stretching, aromatic
1575	C=N stretching
1550	NO_2 asymmetric stretching
1410 , 1360	C-H bending, aliphatic
1340	NO_2 symmetric stretching
1290	C-N stretching
1245	N-N=N stretching
1100 , 1060	characteristic band of tetrazole ring
860	1,4 disubstituted aromatic
720 , 709	C-H bending, aromatic

^{1}H-NMR (dimethyl sulfoxide-d_6)

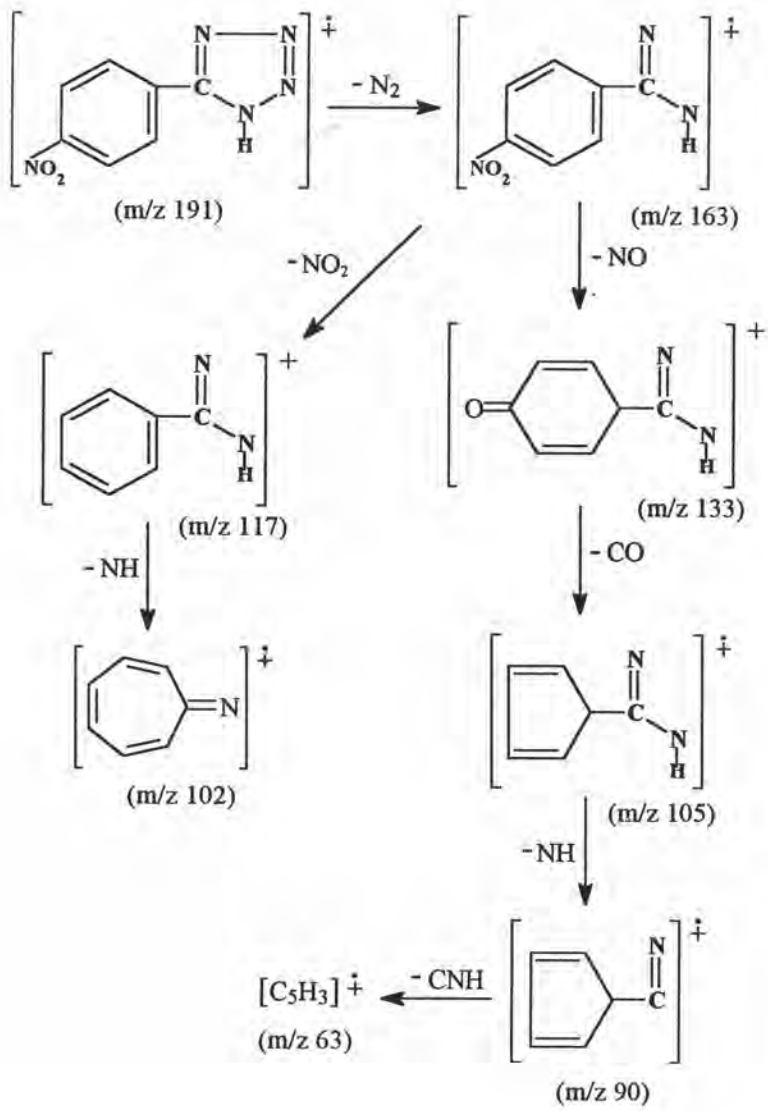


Chemical shift (δ, ppm)	Multiplicity	Position of proton	Number of proton
8.20	d (J = 8.91 Hz)	2′ , 6′	2
8.40	d (J = 8.91 Hz)	3′ , 5′	2
3.80	broad	1	1

^{13}C-NMR (dimethyl sulfoxide-d_6)

Chemical shift (δ, ppm)	Carbon type	Position of carbon
124.5	CH	3′, 5′
128.1	CH	2′, 6′
130.5	C	1′
148.6	C	4′
155.4	C	5

Mass spectum of 2 (MW 191) see in appendix A



3. Preparation of 1-(4″-Nitrobenzyl)-5-phenyltetrazole (3)

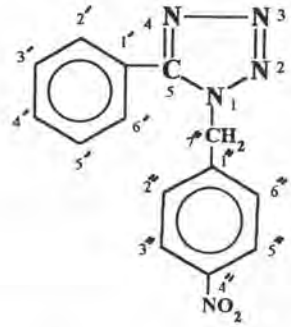
A solution of the potassium salt of 5-phenyltetrazole was prepared by dissolving 2.20 g (1.51×10^{-2} mol) of the 5-phenyltetrazole in small amount of ethanol and adding 1.06 g (7.67×10^{-3} mol) of potassium carbonate and sufficient water to form a clear solution. After adding of 3.25 g (1.51×10^{-2} mol) p-nitrobenzyl bromide the mixture was heated to reflux at 75-80 °C for 4 hours. The product was cooled and recrystallized from methanol. The yield of 3 was 3.69 g (87%), white solid, m.p. 121-122 °C, and spectroscopic data of 3 as shown in page 45-47.

Spectroscopic data of 3

IR ν_{max} (KBr disc)

Wave number (cm^{-1})	Bond type
3080	C-H stretching, aromatic
2950 , 2865	C-H stretching, aliphatic
1610 , 1440	C=C stretching, aromatic
1540	C=N stretching
1520	NO_2 asymmetric stretching
1450 , 1360	C-H bending, aliphatic
1350	NO_2 symmetric stretching
1290	C-N stretching
1245	N-N=N stretching
1100 , 1040	characteristic band of tetrazole ring
860	1,4 disubstituted aromatic
730 , 700	C-H bending, aromatic

^{1}H-NMR (dimethyl sulfoxide-d_6)

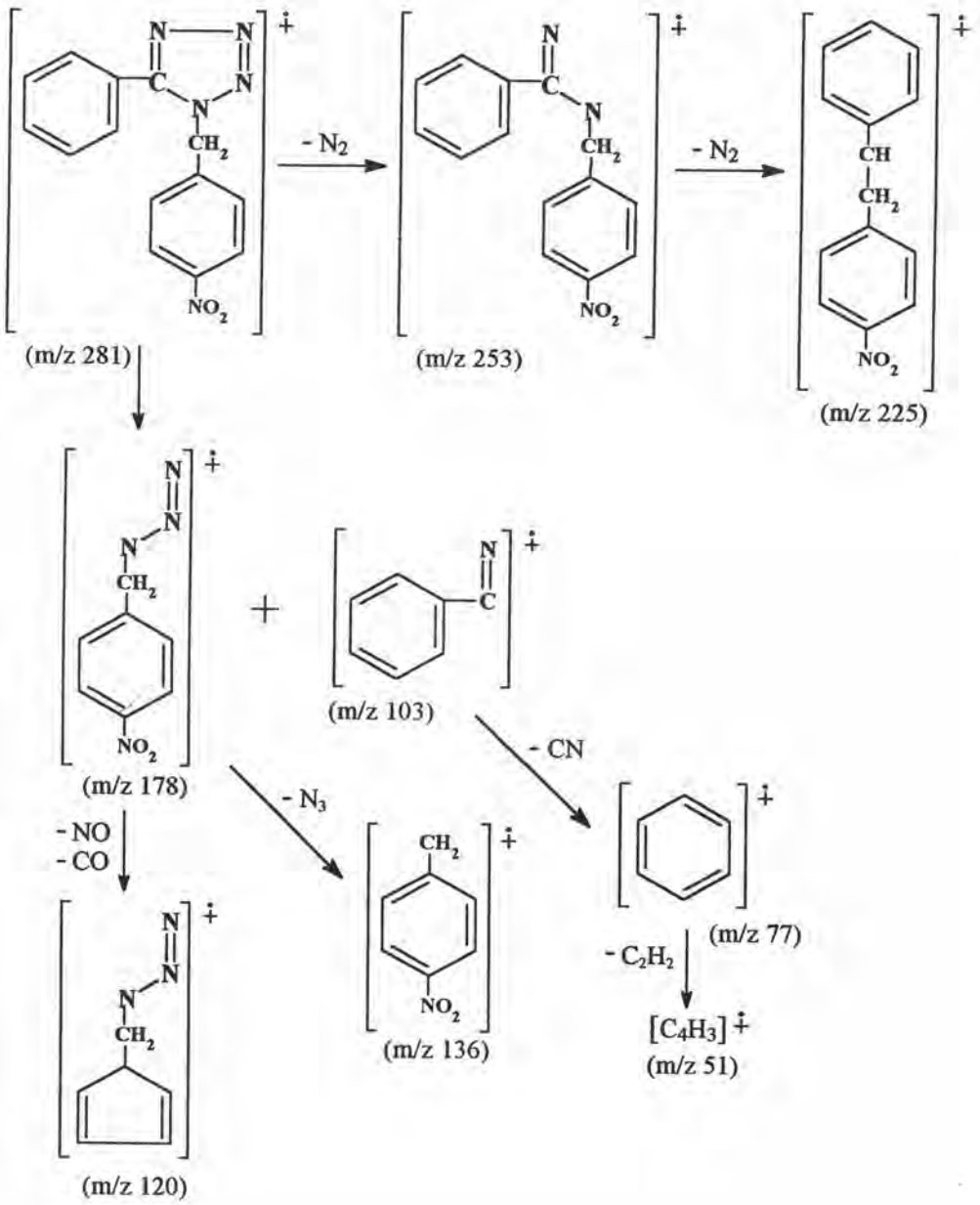


Chemical shift (δ,ppm)	Multiplicity	Position of proton	Number of proton
6.20	s	7″	2
7.52	m	2′, 4′, 6′	3
8.03	m	3′, 5′	2
7.65	d (J = 8.40 Hz)	2″, 6″	2
8.25	d (J = 8.40 Hz)	3″, 5″	2

^{13}C-NMR (dimethyl sulfoxide-d_6)

Chemical shift (δ, ppm)	Carbon type	Position of carbon
128.7	C	1′
126.4	CH	3′, 5′
129.5	CH	2′, 6′
130.7	CH	4′
164.5	C	5
55.1	CH_2	7″
123.8	CH	3″, 5″
129.4	CH	2″, 6″
141.2	C	1″
147.4	C	4″

Mass spectrum of 3 (MW 281) see in appendix A



4. Preparation of 1-(4″-Nitrobenzyl)-5-(4′ nitrophenyl)tetrazole (4)

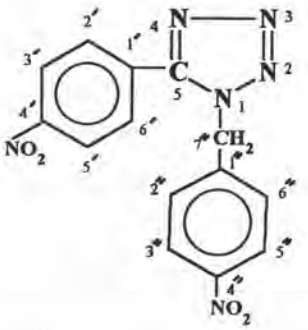
A solution of the potassium salt of 5-(4′-Nitrophenyl)tetrazole was prepared by dissolving 1.01 g (5.28×10^{-3} mol) of the 5-(4′-Nitrophenyl) tetrazole in small amount of ethanol and adding 0.37 g (2.64×10^{-3} mol) of potassium carbonate and sufficient water to form a clear solution. After adding of 1.14 g (5.28×1010^{-3} mol) p-nitrobenzyl bromide the mixture was heated to reflux at 75-80 °C for 3 hours. The product was cooled and recrystallized from methanol. The yield of 4 was 1.34 g (78%), yellow solid, m.p. 192-193 °C and spectroscopic data of 4 as shown in page 48-50.

Spectroscopic data of 4

IR ν_{max} (KBr disc)

Wave number (cm^{-1})	Bond type
3080	C-H stretching, aromatic
2950 , 2865	C-H stretching, aliphatic
1610 , 1440	C=C stretching, aromatic
1540	C=N stretching
1520	NO_2 asymmetric stretching
1450 , 1360	C-H bending, aliphatic
1350	NO_2 symmetric stretching
1290	C-N stretching
1245	N-N=N stretching
1100 , 1040	characteristic band of tetrazole ring
860	1,4 disubstituted aromatic
730 , 700	C-H bending, aromatic

^{1}H-NMR (dimethyl sulfoxide-d_6)

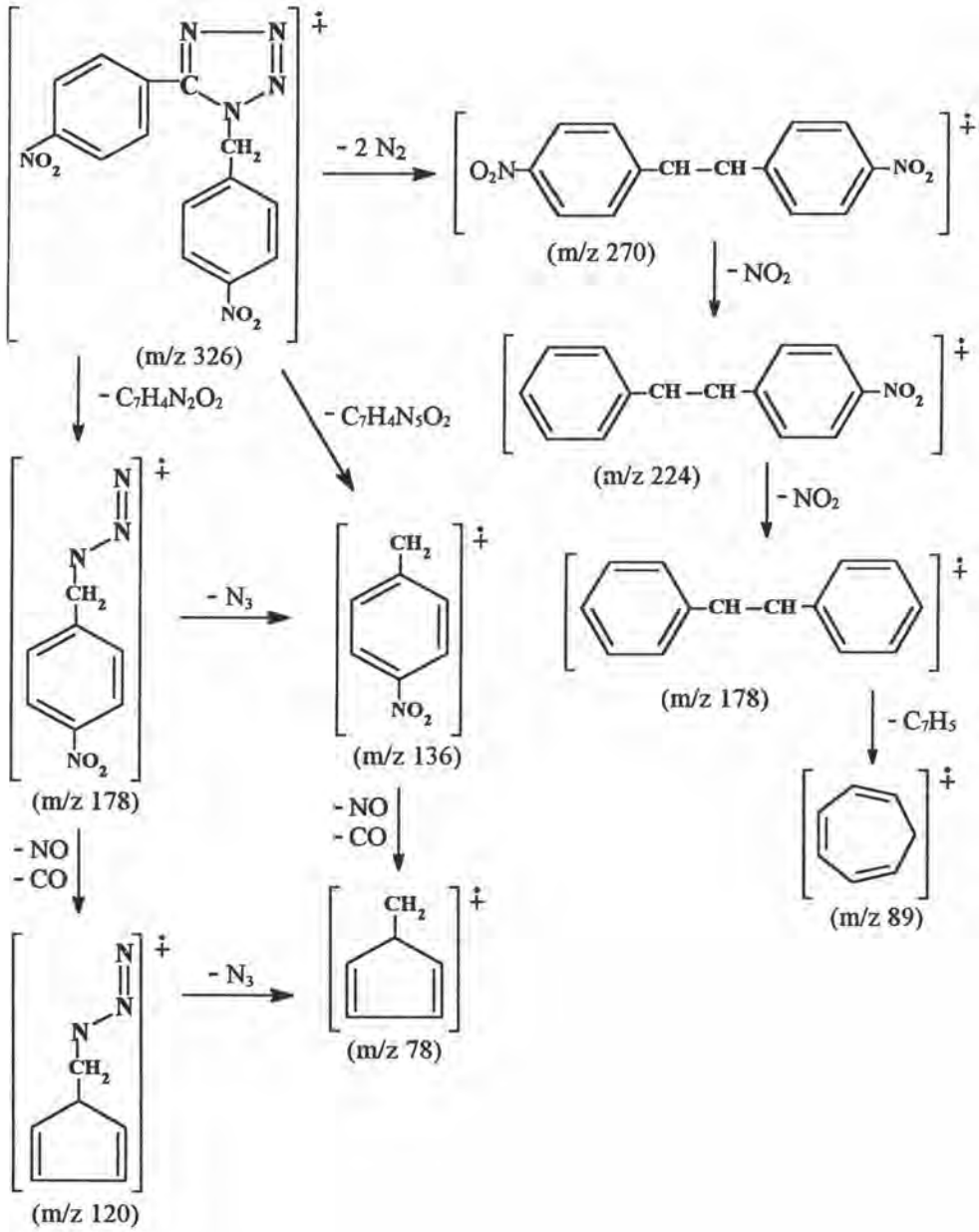


Chemical shift (δ,ppm)	Multiplicity	Position of proton	Number of proton
6.26	s	7″	2
8.25	d (J = 8.44 Hz)	2′, 6′	2
8.38	d (J = 8.44 Hz)	3′, 5′	2
7.65	d (J = 8.60 Hz)	2″, 6″	2
8.30	d (J = 8.60 Hz)	3″, 5″	2

^{13}C-NMR (dimethyl sulfoxide-d_6)

Chemical shift (δ, ppm)	Carbon type	Position of carbon
132.4	C	1′
124.6	CH	3′, 5′
129.7	CH	2′, 6′
148.6	C	4′
162.9	C	5
55.4	CH_2	7″
124.0	CH	3″, 5″
127.7	CH	2″, 6″
140.9	C	1″
147.6	C	4″

Mass spectrum of 4 (MW 326) see in appendix A



Determination of Properties of Diesel Fuel

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

1. Study of effect of alcohol on physical properties of tetrazole derivatives and base diesel fuel and determintion of the physical properties of these alcohol (ethanol, 2-butanol, 1-hexanol and 1-octanol) are as follow:

1. solubility in diesel fuel
2. solubility of tetrazole derivatives in these alcohol
3. cetane index by ASTM D976 of each alcohol
4. flash point of each alcohol in base diesel fuel at 2.5 and 5.0 percent by volume

2. comparison of the effect of these alcohols in (1) and choose one from these alcohols which had little effect value to base diesel fuel.

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

1. The effect of % by volume of 1-hexanol on physical properties of base diesel was blended by varying % by volume of 1-hexanol at 0, 2.5, 5.0, 7.5, 10.0, 15.0, respectively.

2. Determination of the physical properties of base diesel fuel blended with 1-hexanol as follow:

Physical properties:

1. Mid-boiling point	by ASTM D86
2. Flash point	by ASTM D93
3. Cetane index	by ASTM D976
4. API gravity	by ASTM D1298

3. Determination of cetane index of base diesel blended with varying tetrazole derivatives (0.05 % by weight) and 1-hexanol (2.5 % by volume)

Tetrazole derivatives as follow:

1. 5-phenyltetrazole
2. 5-(4′-nitrophenyl)tetrazole
3. 1-(4″-nitrobenzyl)-5-phenyltetrazole
4. 1-(4″-nitrobenzyl)-5-(4′-nitrophenyl)tetrazole

1. Tetrazole derivatives (0.05 % by weight base on density of base diesel fuel) was dissolved in 1-hexanol (2.5 % by volume) and blended with base diesel fuel(2000 cm^3).

2. Determine cetane index of the blended tetrazole derivatives and 1-hexanol in base diesel fuel.

4. Determination of the physical and chemical properties of tetrazole derivatives or octylnitrate (0.05 % by weight) and 1-hexanol (2.5 % by volume) in base diesel fuel as follow:

1. 5-phenyltetrazole
2. 5-(4″-nitrophenyl)tetrazole
3. Octylnitrate

1. Tetrazole derivatives or commercial cetane improver (0.05 % by weight) were dissolved with 1-hexanol (2.5 % by volume) and blended with base diesel fuel (2000 cm^3)

2. Determine of physical properties of this blended base diesel fuel as follow:

Physical properties:

1. Mid-boiling point	by ASTM D86
2. Cetane number	by ASTM D613
3. Cetane index	by ASTM D976
4. API gravity	by ASTM D1298