CHAPTER IV

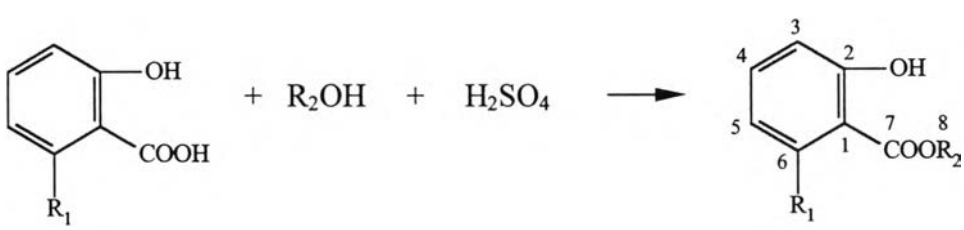
RESULTS AND DISCUSSION

4.1 The CNSL and Esterified-CNSL

The CNSL was obtained by solvent-extraction technique (e.g. n-hexane) from outer shell of cashew nut, which is a dark brown viscous liquid oil, strong acid, insoluble in water, likely soluble in organic solvent, alcohol, ether and petroleum ether.

The esterified-CNSL was obtained by refluxing CNSL and alcohol 10 hrs using concentrated sulfuric acid as catalyst. The product was brown viscous liquid, insoluble in water, soluble in organic solvent, alcohol, ether and petroleum ether. The esterified-CNSL was synthetic to marker dye by coupling reaction with chloroanilines.

The physical properties of CNSL and Esterified-CNSL were studied by the ASTM testing method, as shown in Table 5.



CNSL Esterified-CNSL

Where $R_1 = C_{15}H_{(31-n)}$, $R_2 = C_6H_{13}$

Table 5 : The physical properties of CNSL and Esterified-CNSL.

Test item	ASTM	Result	
		CNSL	CNSL – Ester
Specific Gravity @15.6/15.6°C	D 1298	0.9665	0.9648
Kinematic Viscosity @40°C,cSt	D 445	Too Viscous	15.14
@50°C,cSt	D 445	40.42	11.14
@100°C,cSt	D 445	7.52	3.58
Pour Point, °C	D 97	1	1
Flash Point, (P.M.), °C	D 93	115-120	100-112

The properties of esterified- CNSL were somewhat different from CNSL. For example, the kinematic viscosity at 40, 50, 100^{O}C were changed from too viscous, 40.42, 7.52 in CNSL to 15.14, 11.14 and 3.58 in CNSL-Ester, respectively. The flash point of esterified-CNSL was also lower. As a result, the physical properties of esterified-CNSL was lower than those of CNSL. This is because the ester group makes CNSL-Ester less polar than CNSL.

The characterization of CNSL was accomplished by FT-IR and ^{13}C-NMR tecniques (Figure 1,2). The FT-IR absorption band of CH-streching vibration of aromatic and aliphatic were shown at 3009 and 2926, 2854 cm^{-1}, respectively. The C=O-streching vibration was shown at 1646 cm^{-1} and C-O-streching vibration was shown at 1301 cm^{-1}. The board OH absorption peak was approved at 2800-3600 cm^{-1}.

The ^{13}C-NMR spectrum of CNSL exhibited the chemical shift of COOH at 175 ppm and C-C aromatic carbons at 125-131 ppm.

The esterified-CNSL was characterized by FT-IR and ^{13}C-NMR spectra (Figure 3,4). Their spectra indicated the successful esterification of CNSL with hexanol after refluxing for 10 hrs. The FT-IR absorption of OH (phenolic) streching vibration appeared at 3400 cm^{-1}. The ^{13}C-NMR spectrum of C-O peak was sean at 71 ppm which was characteristic of esterification product. Additional C-O peak at 64 ppm was from excess alcohol.

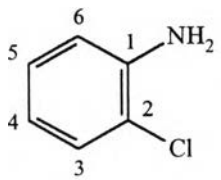
4.2 The chloroaniline

The chloroanilines used in section 3.3.1.2 to prepare chloroaniline diazonium salts was characterized and the FT-IR spectrum and ^{13}C - NMR spectra were shown in Figure (5-16) and the ^{13}C-NMR assignment was tabulated in Table 6 below :

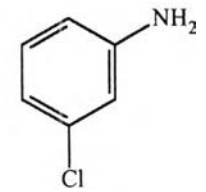
Table 6 : The ^{13}C-NMR spectrum data of chloroaniline.

	Assignments (ppm)					
	C_1	C_2	C_3	C_4	C_5	C_6
2-chloroaniline	142.7	118.9	129.1	118.7	127.4	115.6
3-chloroaniline	147.5	114.5	134.3	117.9	130.0	112.9
4-chloroaniline	144.8	116.0	128.8	122.7	128.8	116.0
2,3-dichloroaniline	144.3	116.8	132.4	119.0	127.2	113.4
2,5-dichloroaniline	143.6	118.6	129.9	117.2	132.9	115.1
3,4-dichloroanilne	145.9	116.1	132.2	120.5	130.4	114.4

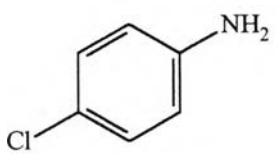
The following cholroaniline compounds used in this study have the formular :



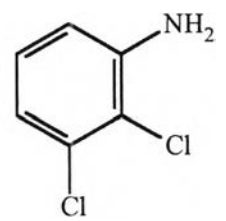
2-Chloroaniline(Compound 1)



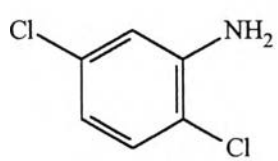
3-Chloroaniline(Compound 2)



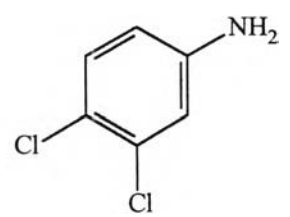
4-Chloroaniline(Compound 3)



2,3-Chloroaniline(Compound 4)



2,5-Chloroaniline(Compound 5)



3,4-Chloroaniline(Compound 6)

4.3 The marker dye.

The Compound 7-12 were marker dyes obtained from coupling reaction of chloroaniline diazonium salt and esterified-CNSL. The products were viscous oil with yellow color.

The physical properties of marker dyes were determined by ASTM method and the results were described in Table 7.

The marker dye Compound 7-12 were characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR that showed in Figure 17-34.

The FT-IR spectrum showed the frequencies at 1586-1599, 3009 and 2855, 2928 cm^{-1} which were characteristic for C=O-streching, CH-streching of aromatic and aliphatic of Compound 7-12.

The ^{13}C-NMR spectrum showed the chemical shifts of C-C aromatic at 125-131 ppm, C-O signal at 71 ppm and the important chemical shift of C-N=N-C signal appeared at 146 and 150 ppm which were characteristic of marker dye of Compound 7-12.

The Compound 13-18 were marker dyes obtained from coupling reaction of chloroaniline diazonium salt and methyl salicylate (Figure 47,48). The characteristic of them was studied by ^{1}H-NMR and ^{13}C-NMR and were shown in Figure 35-48.

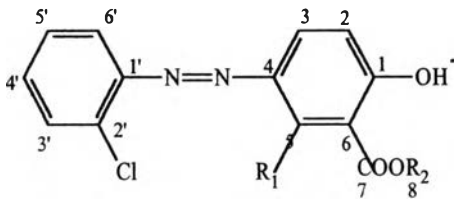
The ^{13}C-NMR spectrum showed the chemical shifts of C-C aromatic 112, 117, 119, 130, 135 and 162 ppm, C-O signal at 52 ppm and COOR signal at 172 ppm.

For the marker dye Compound 13-18, the ^{13}C-NMR spectrum showed the chemical shift of C-C aromatic at 118-133 ppm and C-N=N-C signal at 145,150 ppm which were characteristic of marker dye of Compound 13-18.

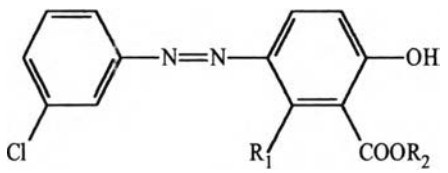
Table 7 : The physical properties of marker dyes Compound 7-12.

Comp.	Test item		
	Specific Gravity @15.6/15.6^{O}C ASTM D 1298	Kinematic Viscosity@50^{O}C,cSt ASTM D 445	Color Visual
Comp.7	0.9720	10.12	yellow
Comp.8	0.9658	9.54	yellow
Comp.9	0.9632	9.33	yellow
Comp.10	0.9712	9.95	yellow
Comp.11	0.9587	9.50	yellow
Comp.12	0.9630	9.78	yellow

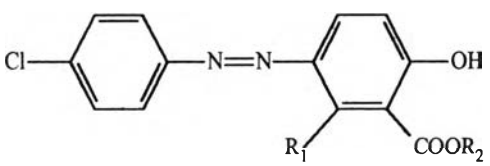
From Table 7, it appeared that all marker dyes gave similar physical properties. For example, the specific gravity was around 0.96-0.97 and kinematic viscosity was 9.33-10.12 cSt. The fact that all marker dyes gave the same yellow color indicated that chloro-substituent on benzene ring did not influence any color change. Nevertheless, the yellow color of marker dyes makes them suitable to be used as both coloring agent for gasoline and the marking agent for diesel because yellow color does not give any significant change in the fuel.



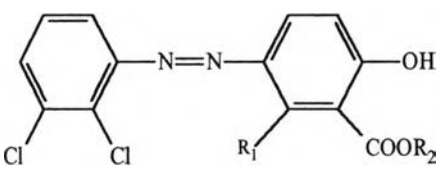
Marker dye (Compound 7)



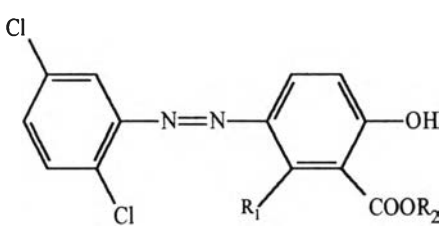
Marker dye (Compound 8)



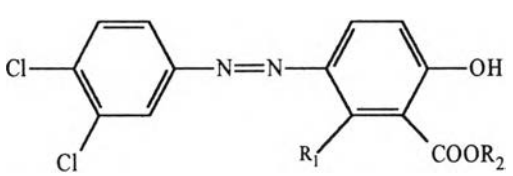
Marker dye (Compound 9)



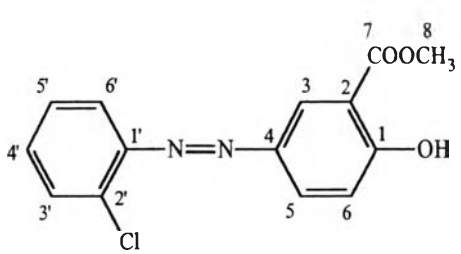
Marker dye (Compound 10)



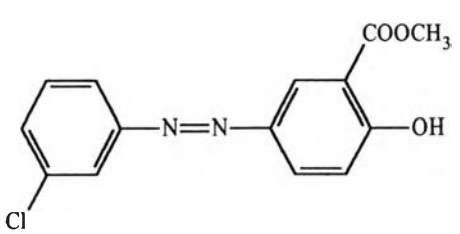
Marker dye (Compound 11)



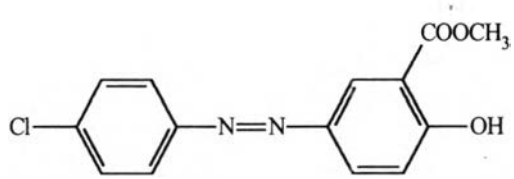
Marker dye (Compound 12)



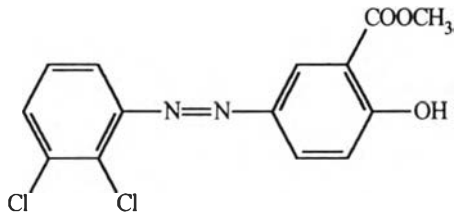
Marker dye (Compound 13)



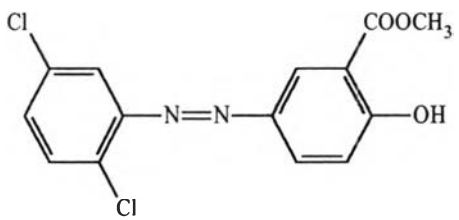
Marker dye (Compound 14)



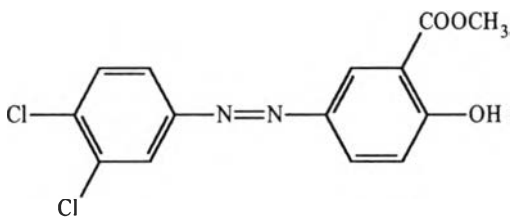
Marker dye (Compound 15)



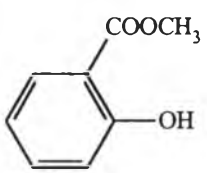
Marker dye (Compound 16)



Marker dye (Compound 17)



Marker dye (Compound 18)



Methyl salicylate (Compound 19)

4.4 Effect of marker dyes to fuel oil

4.4.1 Physical properties of dyed and undyed diesel fuel oil

The physical properties of dyed and undyed diesel fuel oil were determined according to specific ASTM methods. The results are tabulated in Table 8.

Table 8 : The effect of marker dyė (Comp.7) to dyed and undyed diesel fuel

Test Item	ASTM	Limit	Result	
			Dyed	Undyed
API Gravity @ 60 ^{O}F	D 1298	Report	39.4	39.1
Specific Gravity @ 15.6 / 15.6 ^{O}C	D 1298	Report	0.8280	0.8294
Calculated Cetane Index	D 976	47 min	57.3	57.8
Kinematic Viscoscity @ 40 ^{O}C, cSt	D 445	1.8 - 4.1	3.1	3.2
Pour Point , ^{O}C	D 97	10	1	1
Sulfur Content , % Wt	D 4294	0.05	0.03	0.03
Copper Strip Corrosion , Number (3 hrs, @ 50 ^{O}C)	D 130	No. 1	No. 1	No. 1
Flash Point , (P.M) , ^{O}C	D 93	52	72	74
Distillation : (Correct Temp.)	D 86			
IBP , ^{O}C		Report	172.5	172.4
10 % rec., ^{O}C		Report	213.7	213.5
50 % rec., ^{O}C		Report	281.5	281.3
90 % rec., ^{O}C		357 max.	353.6	353.9
Color , ASTM	D 1500	2.0 max.	0.7	L0.5
	Visual	-	yellow	yellow
Total acid Number , mg KOH / g	D 974		0.007	0.001

In Table 8, Compound 7 was used at the treated rate of 30 ppm(vol) compared to undyed diesel fuel oil. The results from Table 8 indicated that the physical properties of dyed fuel were not significantly different from undyed fuel oil. Both of them gave the same distillation, viscosity, specific gravity, corrosion properties.The flash point of diesel fuel was somewhat lower, perhaps due to contamination of unreacted alcohol and toluene from marker dyed stock solution. However, unreacted alcohol and toluene were not significant to physical properties of diesel but they were improved in combustion of diesel fuel because alcohol enhanced the combustion reaction of fuel oil and toluene makes the flash point diesel fuel lower.

Thus, the data in Table 8 indicated that the marker dye could be used in diesel fuel oil without any effect on the property of the oil.

4.4.2 Physical properties of marker dyes in dyed and undyed gasoline

The physical properties of dyed and undyed gasoline were determined according to ASTM methods. The results are tabulated in Table 9.

Table 9 : The effect of marker dye (Comp.7) to dyed and undyed gasoline

Test Item	ASTM	Limit	Result	
			Dyed	Undyed
API Gravity @ 60 ^{O}F	D 1298	Report	50.9	51.3
Specific Gravity @ 60 / 60 ^{O}F	D 1298	Report	0.7758	0.7741
Octane Number				
- Research Method (RON)	D 2699	95	97.2	97.3
Reid Vapor Pressure @ 37.8 ^{O}C ,kpa				
- Oxygenated Blends	D 5191	62 max	55.5	56.2
Copper Strip Corrosion , Number	D 130	No. 1	No. 1	No. 1
(3 hrs , @ 50 ^{O}C)				
Distillation : (Correct Temp.)	D 86			
IBP , ^{O}C		Report	35.1	33.6
10 % Vol. Evaporated , ^{O}C		70 max.	59.6	58.7
50 % Vol. Evaporated , ^{O}C		70 –110	109.1	106.5
90 % Vol. Evaporated , ^{O}C		170 max.	154.7	154.8
End Point , ^{O}C		200 max.	190.9	193.4
Recovery , % Vol		Report	97.8	97.9
Residue , % Vol		2.0 max.	1.0	0.9
Total acid Number , mgKOH / g	D 974		0.005	0.001

From Table 9 the Compound 7 was used at treated rate of 30 ppm by volume to undyed gasoline. The results from Table 9 indicated that the physical properties of dyed gasoline were not significantly different from undyed fuel oil. Their results gave the same specific gravity, research octane number(RON), reid vapor pressure, distillation properties. Therefore, the results in Table 9 indicated that the marker dye could be used in gasoline without any effect on the properties of gasoline.

The results of physical properties of dyed and undyed fuel (diesel fuel and gasoline) from Tables 8 and 9 indicated that the marker dye at the treated rate of 30 ppm (vol.) did not affected physical properties of these fuels. Therefore, the Compound 7-12 can be used as a marker dye in both diesel and gasoline.

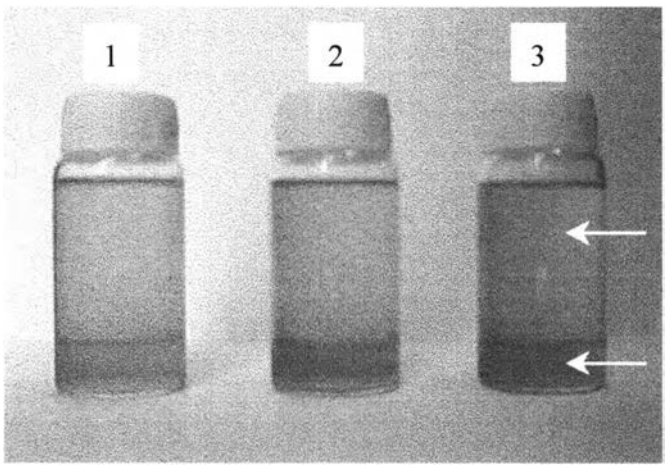
4.5 The suitable extraction solution system

The amount of marker dye in fuel oil was determined by the suitable extraction solution systems which used to extract marker dye obtained from diesel and gasoline fuel oils into the aqueous phase. For exsample, the extraction solution systems such as 1-3% of KOH or NaOH in organic solvent. The absorbance of marker dyes obtained in extracted phase was measured by UV/Vis-spectrophotometer and the results are tabulated in Table 10.

Table 10 : Extraction solution systems.

Solution	Extraction phase – Color	Absorbance
2 % KOH in ethylene glycol	pale – yellow	0.056
2 % KOH in water	Colorless	0.007
2 % KOH in NH_4OH	Colorless	0.003
2 % KOH in acetone	pale - yellow (opaque)	0.224
2 % KOH in methanol	fair – yellow	0.097
5 % KOH in ethylene glycol	pale – yellow	0.086
5 % KOH in methanol	fair – yellow	0.145
10 % KOH in ethylene glycol	fair – yellow	0.189
10 % KOH in methanol	strong – yellow	0.264

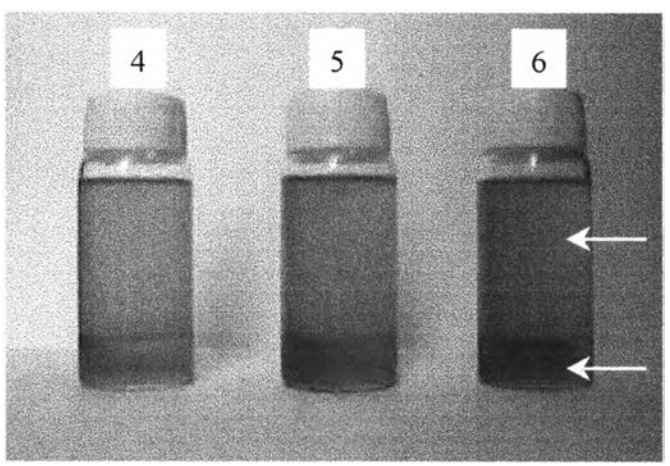
The property of extraction system should be a basic system because those marker dyes contain a phenolic group that exhibits acidic property. The results in Table 10 showed that the 10% KOH in methanol is a suitable extraction solution system because it gave higher absorbance and a strong yellow color in extraction phase. The color of extraction phase of marker dyes Compound 7 to 9 gave a strong yellow phase while marker dyes Compound 10 to 12 gave a strong yellow-orange phase. The extraction system of 2% KOH in water and in NH_4OH including acetone were not suitable because they gave colorless and opaque phases, respectively.



1. Extraction phase of marker dye Compound 7

2. Extraction phase of marker dye Compound 8

3. Extraction phase of marker dye Compound 9



4. Extraction phase of marker dye Compound 10

5. Extraction phase of marker dye Compound 11

6. Extraction phase of marker dye Compound 12

4.6 Treatment and determination of marker dyes in fuel oil

4.6.1 Treatment and determination of marker dyes in diesel fuel oil

The marker dye was used at the treated rate that did not affect on the physical properties of fuel oil at the same time it could be able to be detected in laboratory or field test. For example, it was measured by UV/Vis-spectroscopic technique in laboratory and visual color observation in field test. The quantity of marker dye was determined in aqueous phase according to procedures 3.3.4.1 and 3.3.4.2.

4.6.2 Treatment and determination of marker dyes in gasoline

The amount of marker dye in gasoline was measured by UV/Vis-spectroscopic technique and field test. The determination of marker dyes was carried out according to procedures 3.3.4.1 and 3.3.4.2. The maximum wavelength and standard calibration curve of marker dyes were showed in Figure 35-45.

4.7 Stability of marker dyes in fuel oil

The stability of marker dyes was monitored to measuring the absorption of marker dyes in aqueous extract for a certain period of time by standard calibration curve of UV / Vis-spectroscopy. The results of stability was shown in Tables 11 to 16.

Table 11 : The stability of 30 ppm. marker dye compound 7 in diesel and gasoline

Week	Result in diesel		Ave. result	Result in gasoline		Ave. result
	Result 1	Result 2	(ppm.)	Result 1	Result 2	(ppm.)
1	32.88	33.41	33.14	31.00	31.58	31.29
2	34.05	33.12	33.58	30.36	31.41	30.88
3	31.91	31.33	31.62	31.23	30.01	30.62
4	32.54	31.70	32.12	33.44	30.89	32.16
5	30.23	31.89	31.06	31.51	30.32	30.91
6	31.10	30.51	30.80	30.88	29.52	30.20
7	29.38	29.11	29.24	29.34	30.01	29.67
8	29.87	28.97	29.42	29.90	28.50	29.20
9	28.58	29.04	28.81	29.14	29.63	29.38
10	28.66	28.74	28.7	28.78	28.19	28.48

Table 12 : The stability of 30 ppm. marker dye compound 8 in diesel and gasoline

Week	Result in diesel		Ave. result	Result in gasoline		Ave. result
	Result 1	Result 2	(ppm.)	Result 1	Result 2	(ppm.)
1	32.66	33.53	33.09	31.21	32.57	31.89
2	29.57	30.21	29.89	31.09	32.53	31.81
3	31.87	31.32	31.59	32.88	33.07	32.97
4	30.79	31.06	30.92	30.65	30.44	30.54
5	29.94	31.18	30.56	30.00	30.58	30.29
6	29.11	29.70	29.40	29.41	29.87	29.64
7	28.34	29.01	28.67	28.72	29.24	28.98
8	29.21	28.88	29.04	29.30	28.66	28.98
9	29.04	28.33	28.68	28.09	27.00	27.54
10	28.77	27.89	28.33	28.54	28.35	28.44

Table 13 : The stability of 30 ppm. marker dye compound 9 in diesel and gasoline

Week	Result in diesel		Ave. result	Result in gasoline		Ave. result
	Result 1	Result 2	(ppm.)	Result 1	Result 2	(ppm.)
1	31.82	32.03	31.92	32.01	31.25	31.63
2	31.70	31.14	31.42	31.51	32.02	31.76
3	30.56	32.04	31.30	31.33	30.23	30.78
4	32.57	31.64	32.10	30.83	30.41	30.62
5	30.89	30.24	30.56	30.72	30.01	30.36
6	30.87	29.12	29.99	28.34	29.22	28.78
7	30.55	28.20	29.37	29.92	29.36	29.64
8	28.03	27.98	28.00	28.82	29.07	28.94
9	28.34	28.41	28.37	28.45	27.62	28.03
10	27.55	27.75	27.65	27.39	27.81	27.60

Table14: The stability of 30 ppm. marker dye compound 10 in diesel and gasoline

Week	Result in diesel		Ave. result	Result in gasoline		Ave. result
	Result 1	Result 2	(ppm.)	Result 1	Result 2	(ppm.)
1	31.88	32.43	32.15	30.69	32.52	31.60
2	31.59	32.15	31.87	32.05	31.24	31.64
3	31.07	30.52	30.79	31.25	30.41	30.83
4	30.13	30.50	30.31	30.22	30.30	30.26
5	30.20	30.01	30.10	29.40	29.88	29.64
6	29.84	30.04	29.94	30.07	29.01	29.54
7	29.72	28.11	28.91	28.52	29.11	28.81
8	28.34	28.22	28.28	28.08	28.00	28.04
9	28.03	27.41	27.72	28.05	27.29	27.67
10	27.11	27.55	27.33	27.80	27.14	27.47

Table15 :The stability of 30 ppm. marker dye compound 11 in diesel and gasoline

Week	Result in diesel		Ave. result	Result in gasoline		Ave. result
	Result 1	Result 2	(ppm.)	Result 1	Result 2	(ppm.)
1	32.30	32.74	32.52	31.12	31.32	31.22
2	31.49	31.17	31.33	31.20	31.55	31.37
3	30.02	30.81	30.21	31.47	31.42	31.44
4	30.76	29.90	30.33	30.38	30.71	30.54
5	29.40	30.35	29.87	29.56	29.04	29.30
6	30.11	29.82	29.96	28.12	29.41	28.76
7	29.05	29.01	29.03	28.00	28.09	28.05
8	28.48	28.24	28.36	27.32	28.38	27.85
9	28.30	28.56	28.43	27.55	27.49	27.52
10	27.54	27.13	27.33	27.81	27.19	27.50

Table 16:The stability of 30 ppm. marker dye compound 12 in diesel and gasoline

Week	Result in diesel		Ave. result	Result in gasoline		Ave. result
	Result 1	Result 2	(ppm.)	Result 1	Result 2	(ppm.)
1	31.82	31.04	31.43	30.92	30.34	30.63
2	31.11	31.53	31.32	31.55	30.40	30.97
3	30.01	30.23	30.12	30.73	30.26	30.49
4	30.21	29.88	30.04	30.03	29.83	29.93
5	29.12	29.39	29.25	29.23	28.19	28.71
6	28.66	29.24	28.95	29.57	29.07	29.32
7	29.02	29.52	29.27	28.22	28.61	28.41
8	28.13	28.80	28.46	27.07	28.72	27.89
9	28.36	28.47	28.41	27.82	27.63	27.72
10	28.01	27.59	27.80	27.10	27.30	27.20

The stability of each marker dye which added into diesel and gasoline and kept in dark area was shown in Tables 11 to 16. After ten weeks, the amount of marker dye was 3-4 ppm less than original. Therefore, the marker dyes obtained in this study were stable for at least ten weeks which was enough for the shelf-life of fuel before being consumed on the market.