CHAPTER IV

RESULT

4.1 CHEMICAL FINGERPRINT OF PETRONAS RON 95 (SPECIFIC OBJECTIVE 1)

The first objective was to determine the chemical fingerprint of Petronas RON 95. A total of fifteen samples were prepared and was represented by Petronas A (i-iii) to Petronas E (i-iii). Each of the samples mentioned were analyzed in triplicate using GC-FID. From these analyses, 45 chromatograms were the further analyzed statistically. The number of peaks obtains from each sample is listed in Table 4.1. Figure 4.1 shows the typical GC-FID chromatogram of Petronas C-i-1.

Table 4.1: Number of peaks for samples in first objective

Sample	Replicate	No. of Peak		
		1st injection	2nd injection	3rd injection
Petronas A	i	102	99	100
	ii	85	84	82
	iii	89	83	87
Petronas B	i	88	85	80
	ii	75	91	79
	iii	93	97	90
Petronas C	i	90	89	89
	ii	93	91	74
	iii	69	94	84
Petronas D	i	67	89	89
	ii	71	91	97
	iii	93	94	98
Petronas E	i	101	89	98
	ii	96	65	98
	iii	88	96	94

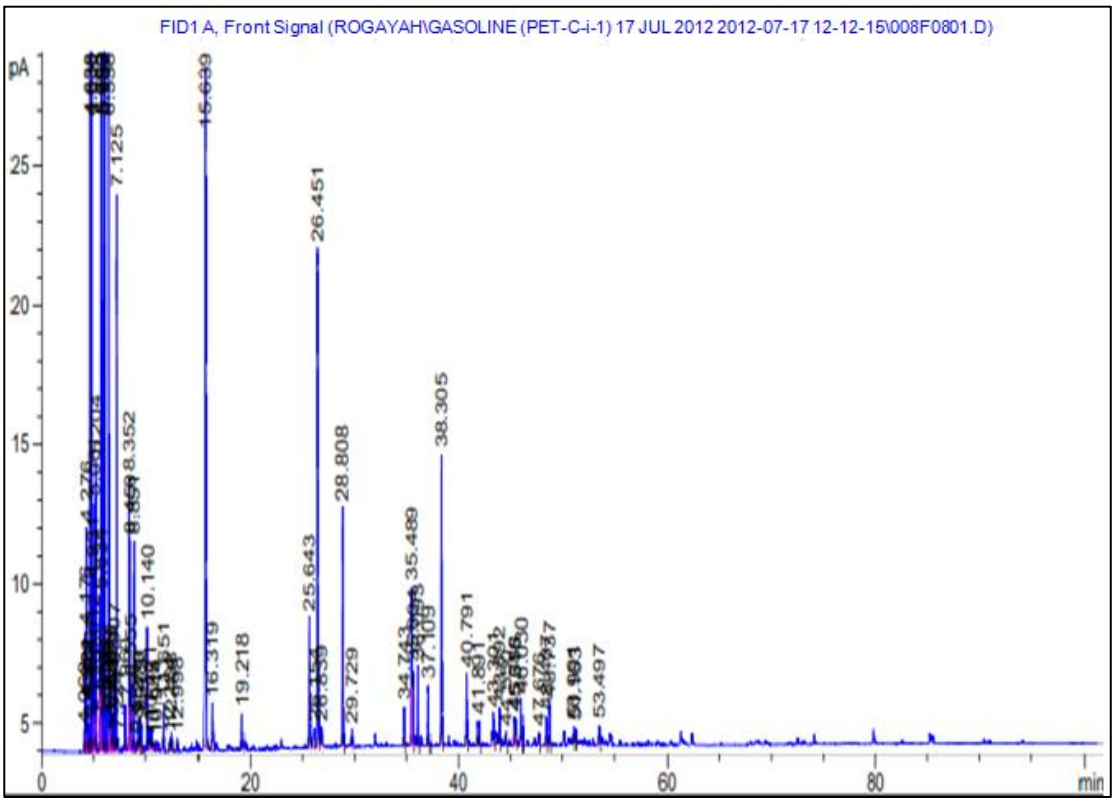

Figure 4.1: Typical chromatogram of Petronas C-i-1

4.2 CHEMICAL FINGERPRINT OF SHELL RON 95 (SPECIFIC OBJECTIVE 2)

The second objective was to determine the chemical fingerprint of Shell RON 95. The numbers of peaks for each chromatogram ranged from 58 to 94. These peaks were much less compared to Petronas petrol chromatogram. However, distribution of peak signal shows a similar trend as Petronas petrol (Figure 4.2). The numbers of peaks for each sample of RON 95 from Shell petrol are shown in detail in Table 4.2.

Table 4.2: Number of peaks for samples in second objective

Sample	Replicate	No. of Peak		
		1st injection	2nd injection	3rd injection
Shell A	i	66	79	72
	ii	86	76	63
	iii	87	83	81
Shell B	i	84	77	80
	ii	74	90	74
	iii	78	78	71
Shell C	i	65	68	74
	ii	71	85	65
	iii	66	90	87
Shell D	i	94	90	75
	ii	94	70	79
	iii	73	74	76
Shell E	i	77	82	58
	ii	68	85	90
	iii	92	71	70

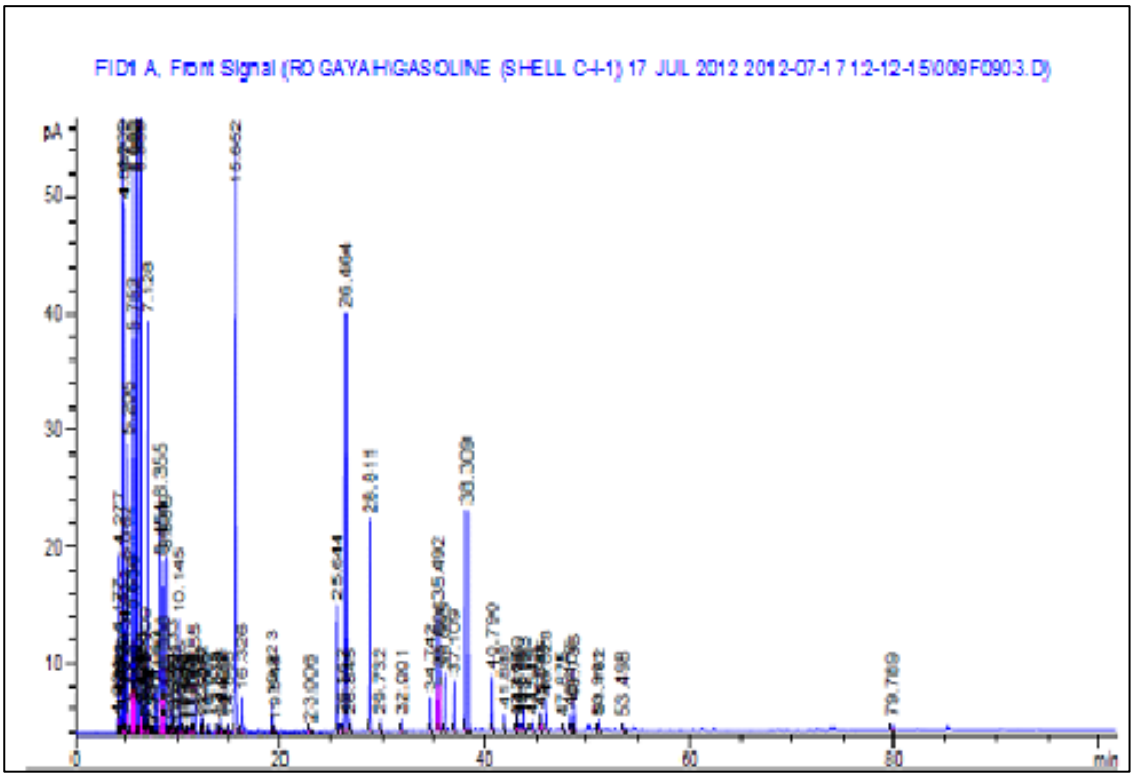

Figure 4.2: Typical chromatogram of Shell C-i-1

4.3 CHEMICAL FINGERPRINT OF BHP RON 95 (SPECIFIC OBJECTIVE 3)

Third objective was to determine the chemical fingerprint of RON 95 from BHP petrol. The highest number of chromatograms peaks identified was 85.This was from BHP B-iii-2. Other samples had given peaks with an average of about 60 to 70 peaks/chromatogram (Table 4.3). It was noted that, BHP RON 95 was chromatographically different compared to RON 95 from Petronas and Shell petrol. This was held true based on their peaks signal at first 10 min. Figure 4.3 shows a typical chromatogram from sample BHP B-iii.

Table 4.3: Number of peaks for samples in third objective

Sample	Replicate	No. of Peak		
		1st injection	2nd injection	3rd injection
BHP A	i	76	80	71
	ii	76	80	66
	iii	83	81	68
BHP B	i	78	71	75
	ii	68	76	71
	iii	67	85	79
BHP C	i	73	80	74
	ii	65	66	75
	iii	84	68	69
BHP D	i	68	75	69
	ii	65	75	70
	iii	79	76	75
BHP E	i	80	68	65
	ii	74	74	63
	iii	76	75	69

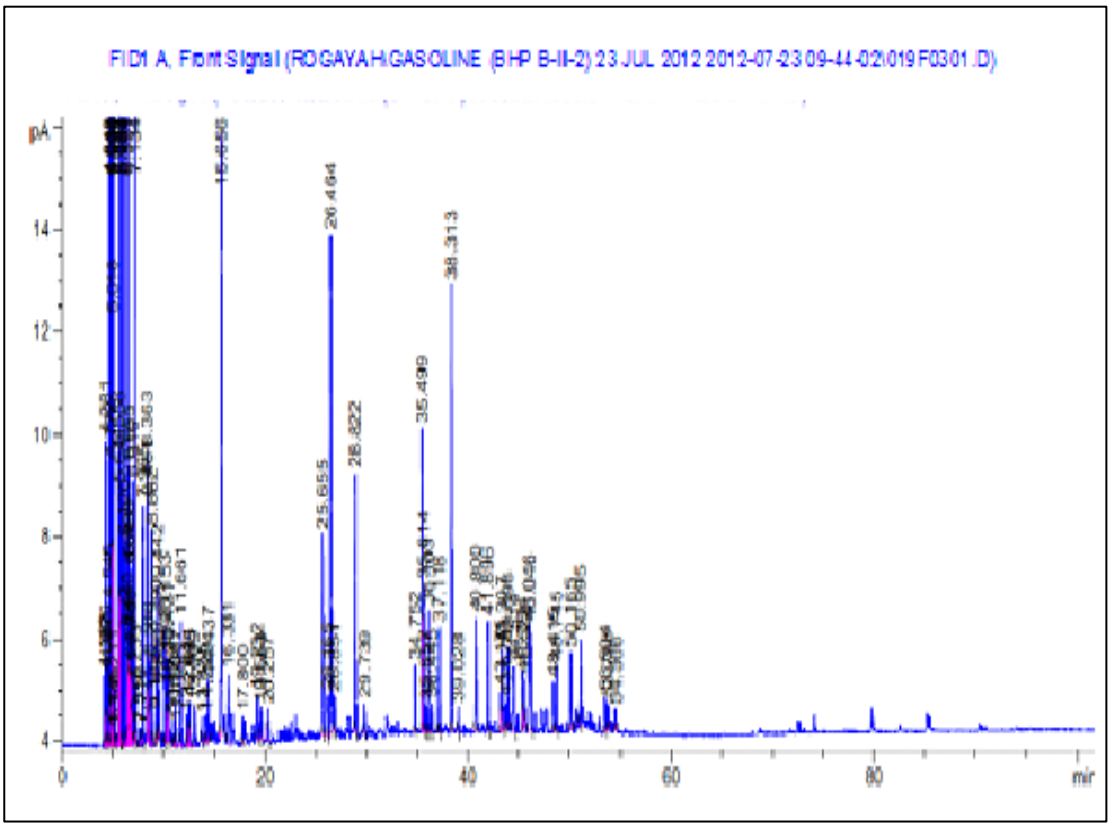

Figure 4.3: Typical chromatogram of BHP B-iii-2

4.4 CHEMOMETRIC ANALYSIS OF SAMPLES FOR OBJECTIVE 1-3

The GC-FID data obtained from the 45 RON 95 petrol samples (n = 3 aliquots x 45 samples = 135 chromatograms) were analyzed by chi-square analysis to investigate the differences between three major commercial petrol in Malaysia. The detail results are given in Table 4.4. From the analysis, it was found that out of 1027 peaks, only 100 were identified as a potential peaks signal to determine the chemical fingerprint of RON 95 based on its suppliers (Petronas, Shell and BHP).

Besides the chi-square test, total of 100 potential peaks signal was performed a PCA analysis to determine the relevant peaks that represent chemical fingerprint for each three brand of petrol. Unfortunately, no positive results were obtained due to the complexity of the GC-FID data.

Due to the no positive results obtained from PCA analysis, all GC-FID data then was analysis by using QUEST modeling C5.0 SPSS Clementine 11.0 version software. The detail results are given in Table 4.5. Based on the results obtained from these analyses, it was found that the results were highly consistent.

Table 4.4: Identified retention time for RON 95 from Petronas, Shell and BHP petrol

Ret. time	Ret. time	Ret. time	Ret. time	Ret. time	Ret. time
4.00	7.20	10.85	20.20	38.25	50.15
5.05	7.50	11.15	22.95	38.30	50.95
5.10	9.00	12.20	26.10	38.35	51.15
5.15	9.05	12.35	26.15	39.00	51.20
5.25	9.10	12.45	26.40	43.15	52.85
5.45	9.20	12.50	26.45	43.55	53.45
5.50	9.25	12.55	26.80	43.65	53.75
5.60	9.35	12.95	28.75	44.45	54.55
5.65	9.40	13.75	28.80	44.50	55.40
5.70	9.50	13.80	29.70	45.35	61.20
6.25	9.55	14.20	31.95	45.50	61.25
6.30	9.95	14.40	35.55	45.60	62.35
6.33	10.30	14.85	35.60	46.00	74.05
6.45	10.35	15.95	35.80	47.65	79.05
6.60	10.40	17.75	36.40	48.35	79.80
6.65	10.55	18.00	37.05	48.40	
6.70	10.60	19.20	37.10	50.10	

Table 4.5: QUEST modeling analysis results

Training		Testing		Validation	
Portion	%	Portion	%	Portion	%
Correct	100	Correct	96.2	Correct	93.3
Wrong	0	Wrong	3.8	Wrong	6.7

Referring to the branched obtained from these analysis (Figure 4.4), a relevant standard retention time that represent the chemical fingerprint of RON 95 petrol for Petronas , Shell and BHP are shown in detail in Table 4.6.

Table 4.6: Relevant retention time for Petronas, Shell and BHP

Brand	**Relevant retention time (min)**	**Peak area**	**%**
Petronas	5.25	< = 0.000	100.000
	6.70	< = 0.809	48.837
	9.20	> 0.000	100.000
	10.25	< = 0.000	50.000
	22.95	> 1.934	75.000
Shell	5.25	> 0.000	100.000
	5.60	> 0.000	100.000
	6.70	< = 0.809	48.837
	9.20	< = 0.000	87.500
	10.25	< = 0.000	50.000
	22.95	< =1.934	100.000
BHP	5.60	< =0.000	100.000
	6.70	> 0.809	95.833
	10.25	> 0.000	100.000

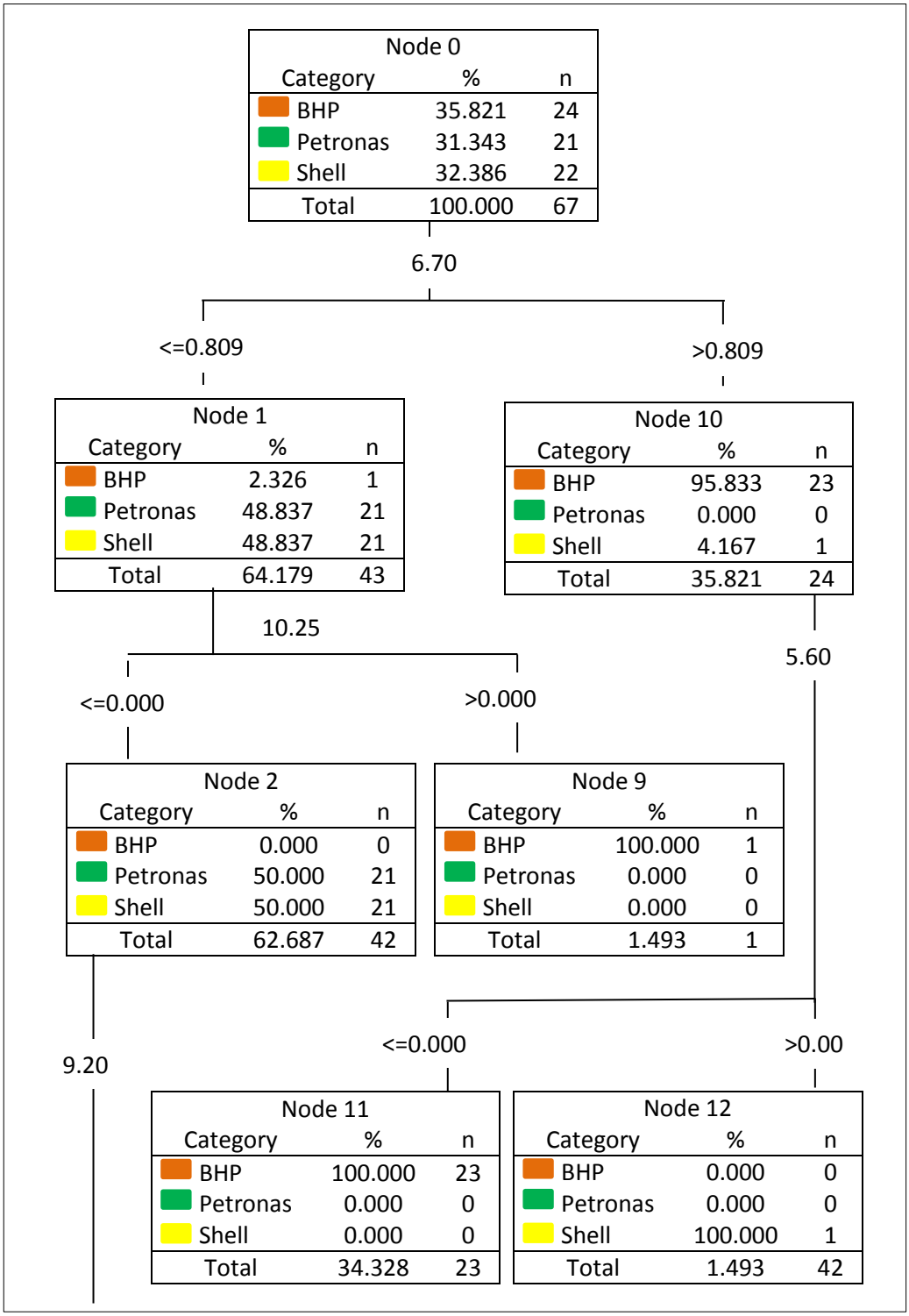

Figure 4.4: QUEST modelling

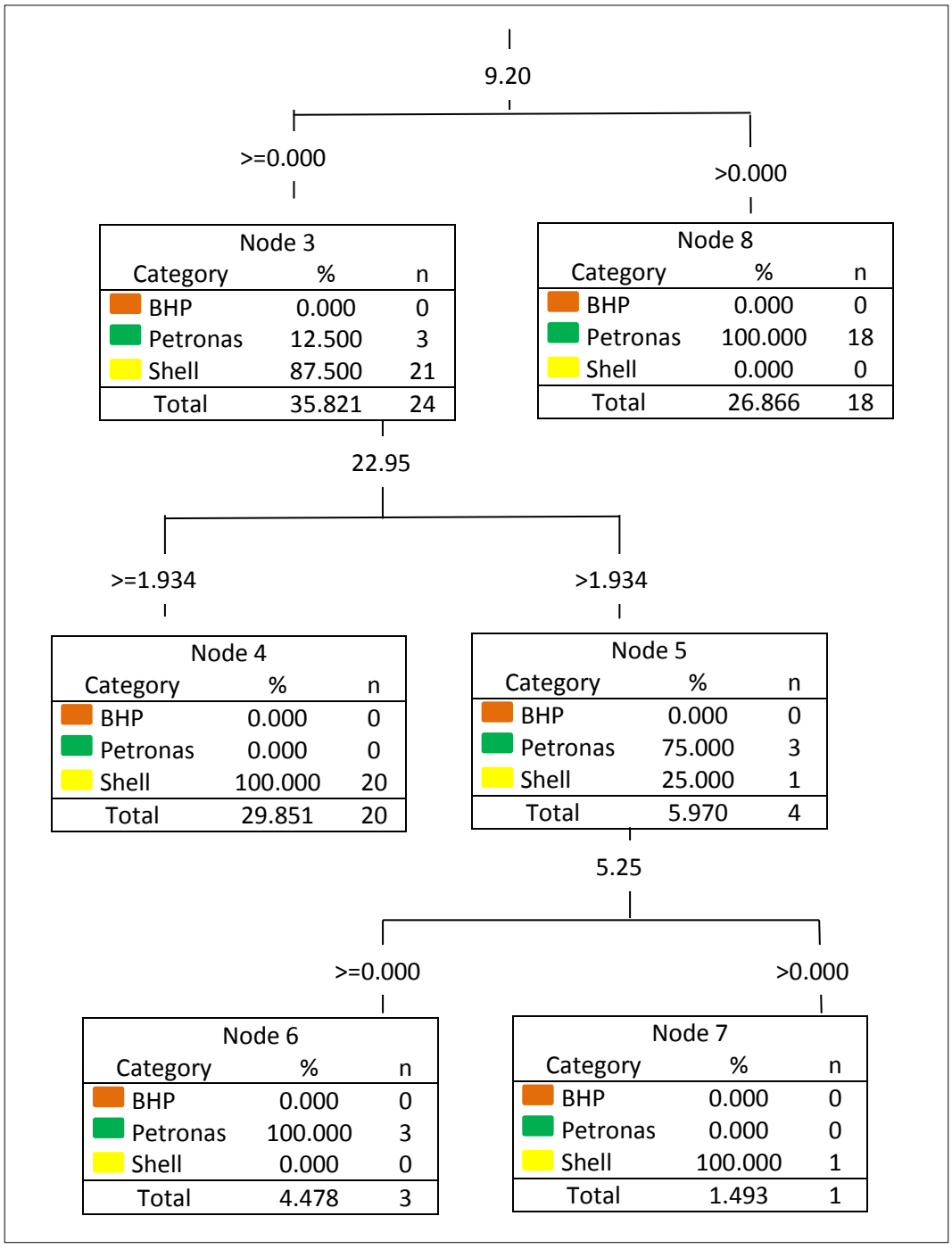

Figure 4.4: QUEST modelling

4.5 UNIQUE CHEMICAL FINGERPRINT OF RON95 BASED ON PETROL STATIONS (4TH OBJECTIVE)

4.5.1 Analysis of Petronas RON 95 petrol

Chi-square analysis was performed to identify unique retention time for RON 95 from various Petronas petrol stations. However, there is no unique retention time identified.

4.5.2 Analysis of Shell RON 95 petrol

Table 4.6 shows the possible unique retention time of chemical within the Petronas RON 95 based on different five service stations within the Klang Valley area. A total of 39 peaks were selected. All peaks had come out within 4.00 to 62.35 min of the chromatogram. Further statistical analysis using chi-square test had truly indicated that the peaks were important chemical fingerprints that would allow anyone to identify the source of RON 95 Shell petrol station.

Table 4.7: Identified retention time of RON 95 for Shell petrol

Ret. Time	Ret. Time	Ret. Time	Ret. Time	Ret. Time
4.00	9.55	12.50	31.95	48.40
5.25	10.30	13.75	35.55	48.70
5.60	10.35	13.80	35.60	50.95
5.65	10.40	14.20	37.05	51.15
7.50	10.60	14.40	37.10	53.45
7.65	10.85	14.85	45.35	61.20
9.10	11.00	19.50	45.50	62.35
9.50	11.15	29.70	46.00	

PCA analysis was employed to investigate the relevant peaks that represent the chemical composition of the each RON 95 Shell petrol from different service station. Unfortunately, no positive results obtained from these analyses.

4.5.3 Analysis of BHP RON 95 petrol

GC-FID data were obtained from 15 samples of RON 95 BHP petrol. The chromatogram data were then analyzed using chi-square test. The results are shown in detail in Table 4.8. Only 16 retention time was identified as unique and able to identify specific BHP service station.

Table 4.8: Identified retention time of RON 95 for BHP petrol

Ret. time	Ret. time	Ret. time
4.00	10.35	37.05
5.05	10.40	37.10
7.50	13.75	45.50
9.10	13.80	54.50
9.50	14.20	
9.55	14.85	

PCA analysis was employed to investigate the relevant peaks that represent the chemical composition of the each RON 95 BHP petrol from different service station. Unfortunately, no positive results obtained from these analyses.