A RAPID GAS CHROMATOGRAPHY METHOD FOR SIMULTANEOUS DETERMINATION OF LPG COMPOUNDS

METODE GAS KROMATOGRAFI CEPAT UNTUK PENENTUAN SENYAWA LPG SECARA SIMULTAN

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ABSTRAK

Sebuah metode kromatografi gas cepat menggunakan kolom HP Plot/Al_2O_3 untuk penentuan tiga belas senyawa pada standar LPG (Liquefied Petroleum Gas) (etana, propana, propilena, iso-butane, n-butana, trans-2-butena, 1-butena, isobutilena, neo-pentana, cis-2-butena, iso-pentana, n-pentana, 1,3 butadiena) telah dikembangkan. Komponen-komponen LPG dipisahkan dalam waktu sekitar 8 menit dengan menggunakan program elusi gradien dengan menggunakan helium sebagai gas pembawa pada laju alir 5 mL menit^{-1}. Standar deviasi relatif (RSD) untuk konsentrasi masing-masing komponen LPG berkisar antara 0,27-1,91%. Metode ini telah digunakan untuk penentuan 10 sampel LPG. Dari hasil analisa didapatkan bahwa komposisi sampel LPG memenuhi spesifikasi mutu LPG di Indonesia untuk masing-masing parameter yaitu C2 <0,8% mol, C3 + C4> 97% mol dan C5 +. <2,0% mol.

Kata kunci: kromatografi gas, LPG, kolom HP Plot/Al_2O_3

ABSTRACT

A rapid gas chromatography method using a HP Plot/Al_2O_3 column for the determination of thirteen compounds of LPG (Liquefied Petroleum Gas) standard (ethane, propane, propylene, iso-butane, n-butane, trans-2-butene, 1-butene, isobutylene, neo-pentane, cis-2-butene, iso-pentane, n-pentane, 1,3 butadiene) was developed. The LPG components were separated in about 8 min by gradient elution program and helium was used as a carrier gas at a flow rate of 5 mL min^{-1}, The relative standard deviation (RSD) for the LPG standard concentration were found to range between 0.27-1.91 % . The method had been applied to the determination of the 10 LPG samples. The composition of analyzed samples have comply with the Indonesian LPG specification for each parameter (C_2<0.8 % mol, C_3+C_4>97 % mol and C_{5+}.<2.0 % mol).

Keywords: *gas chromatography, LPG, HP Plot/Al_2O_3 column*

I. INTRODUCTION

LPG (Liquefied Petroleum Gas) as a fuel for household and industrial interests that indispensable in Indonesia. Based on LPG consumption data through 2012, it was known that the need of the LPG consumption in the household sector about 70% of the national LPG requirements. Meanwhile the industrial and transportation sectors just utilized as much as 30% of national LPG need. It is estimated that LPG needs of the household sector will increase by 2% per year[1].

Liquefied petroleum gas (LPG) obtains from petroleum refining and natural gas that liquefied by certain process. In petroleum refining, LPG is collected during distillation, as lighter compounds dissolved in the crude oil, as well as generated in the cracking process of heavy hydrocarbons. Cracking process conducted by two ways i.e thermal and catalytic cracking that the large hydrocarbon molecules are broken down into smaller and more useful ones: Therefore, LPG products from cracking process will contained the unsaturated hydrocarbon such as 1,3 butadiene, cis-2 butene, isobutene, iso butilene etc[2].

LPG has a different chemical compound to natural gas even though they are both hydrocarbons, this gas is colorless, typically comprised of mainly propane (C_3H_8), butane (C_4H_{10}), or a combination of these two constituents[3].

Measurement of LPG has evolved over the past several years from the straightforward volumetric form of measurement to the more sophisticated and more accurate mass measurement systems being used in virtually all LPG custody-transfer applications. In mass-measurement systems, metered volumes of product are multiplied by the product density at flowing pressure and temperature to arrive at the measured mass of product. As the term implies, however, the result of this type of measurement is a mass of product, not its volume[4].

Because LPG is commonly bought and sold by volume, the measured mass must be converted to volume so that accounting can be completed. To make this conversion, a representative sample of the product delivered over the specified accounting period must be secured and analyzed by gas chromatography to obtain a compositional breakdown[4].

Gas chromatography (GC), is a common type of chromatography used in analytical chemistry for separating and analyzing compounds that can be vaporized without decomposition. Typical uses of GC include testing the purity of a particular substance, or separating the different components of a mixture[5].

Generally, gas chromatography (GC) is the most popular method for the analysis of natural gas and LPG[6-12]. In this method, the stationary phase is based on particulate packing materials. Particulate packing materials, however, can also causing backpressures when higher flow rates are attempted. Separation times of around 20 minutes or more is often required. Therefore, it is needed a rapid separation by developing certain column. One of developed column is HP Plot that contain capillary materials such as polystyrene divinylbenzene/ethylene glycol dimethacrylate coated onto a fused silica capillary. It is suitable for analyzing: of hydrocarbons (natural gas, refinery gas, C1-C7, all C1-C3 isomers and saturated hydrocarbon, like propene, butadiene etc)

HP PLOT represents an innovative type of column for rapid chromatographic analysis. In contrast to the conventional GC columns, HP Plot columns are formed from a single piece of porous silica gel, thus giving them greater porosity and permeability, allowing chromatographic analyses to be performed in a fraction of the time previously required[13].

In the present study, a new GC method by using a HP Plot column was developed for the simultaneous determination of LPG components

II. MATERIALS AND METHODS

A. Materials

LPG standard was purchased from PT. Air Liquid Indonesia that contains of ethane, propane, propylene, iso-butane, n-butane, trans-2-butene, 1-butene, isobutylene, neo-pentane, cis-2-butene, iso-pentane, n-pentane and 1,3 butadiene components. 10 samples of LPG to be analyzed i. e the typical of LPG from natural gas and LPG from oil refinery products.

B. Instrumentation

The GC system consisted of dual channel design supports inlet and Flame ionization detector (FID) (Agilent Technologies, Inc, USA). Electronic flow/ pressure control:0.0 to 100 psig pressure range, 0.0 to 100.0 mL/min. Ranges are chosen to provide optimum performance over normal packed column set point ranges. The mobile phase comprises of helium, hydrogen and compressed air. HP plot/ Al_2O_3 film thickness, HP part No. 1909 IP-S-15, US Patent No. 4,293,415 (50 m x 0.32 mm x 8.0 µm) columns was used.

C. Experimental/Methods

GC analyses were performed on a 6890 GC System (Agilent Technologies, USA) equipped with a split/splitless (1:100) capillary injector and a FID. The air, hydrogen and Helium flow to the detector were kept at 200, 30 and 5 mL min^{-1}, respectively. The temperature of the injector and detector was at 200 ^{o}C. The oven was set using temperature program from 30-50 ^{o}C, with ramp temperature at 10^{o}C min^{-1} and held for 5 min at 150^{o}C. The peak areas were used to calculate the levels of the analytes. Calibration was carried out by analysing a gas mixture of known composition and the quantification of the analytes was based on the peak area using the external calibration method.

III. RESULT AND DISCUSSION

A. Gas Chromatography Method Development

1. Effect of flow rate

The effects of flow rates (3, 4, 5 and 6 mL min-1) on the separation of the analytes were studied. The retention times became progressively shorter as the flow rate was increased (Figures. 1a, b, c and d). When the flow rate 3 and 4 mL min-1 were used, neo-pentane (peak 9) and cis-2-butene (peak 10) were not well resolved (Figure 1A and B). The fourth flow (6 mL min-1) was given the shortest time separation but this would need larger amount of mobile phase. The third flow (5 mL min^{-1}) provided good separation of the components below 10 min (Figure 1C), and was chosen for this study as it gave better retention time and adequate amount of mobile phase consumption. The order of elution was:

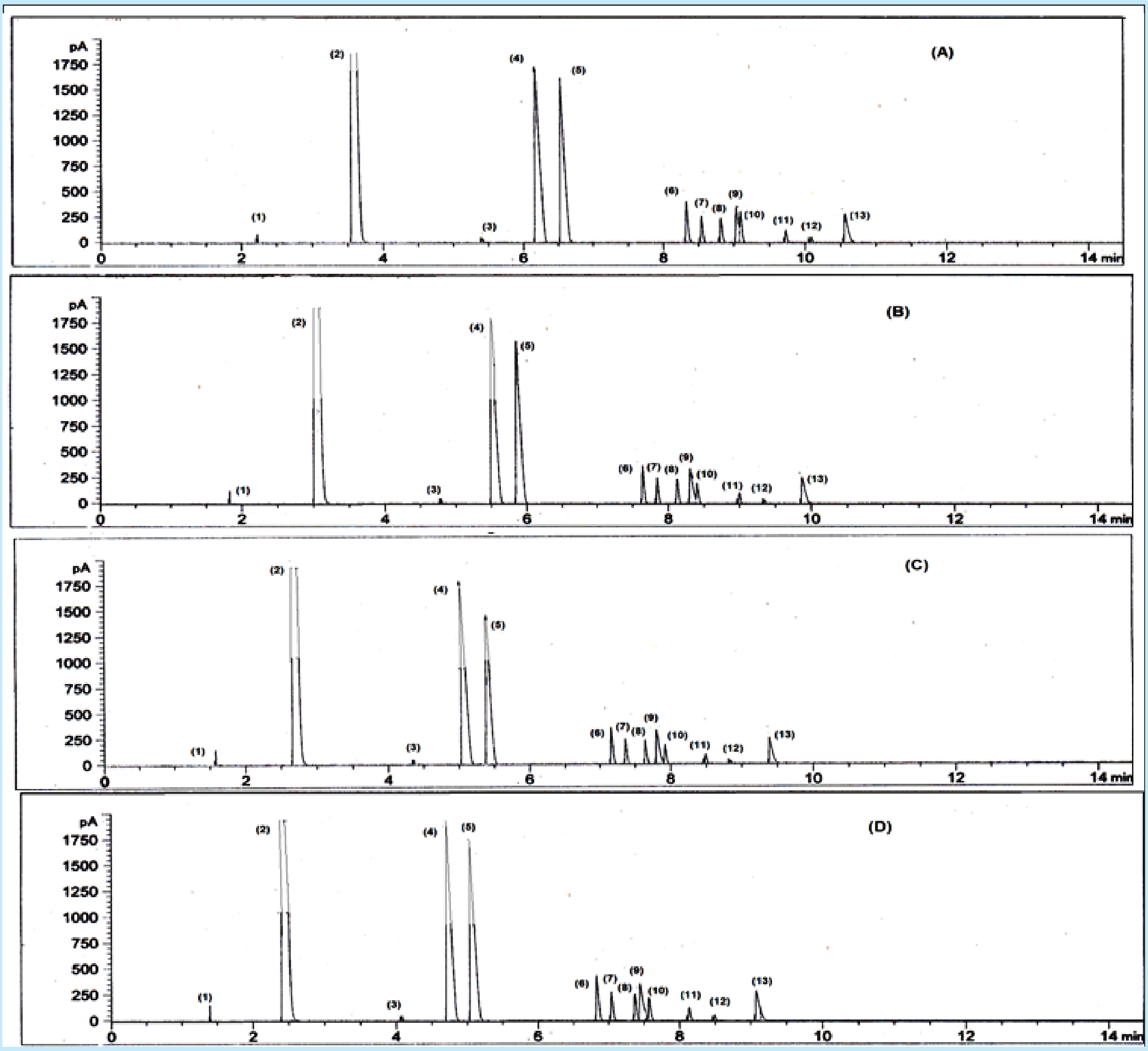

Figure 1
The effect of flow rate on the GC separation of LPG standard using HP plot/ Al2O3 column using flow rate of (A) 3, (B) 4, (C) 5 and (D) 6 mL min^{-1}. Peak assignment: (1) ethane, (2) propane, (3) propylene, (4) iso-butane, (5) n-butane, (6) trans-2-butene, (7) 1-butene, (8) isobutylene, (9) neo-pentane, (10) cis-2-butene, (11) i-pentane, (12) n-pentane and (13) 1,3 butadiene

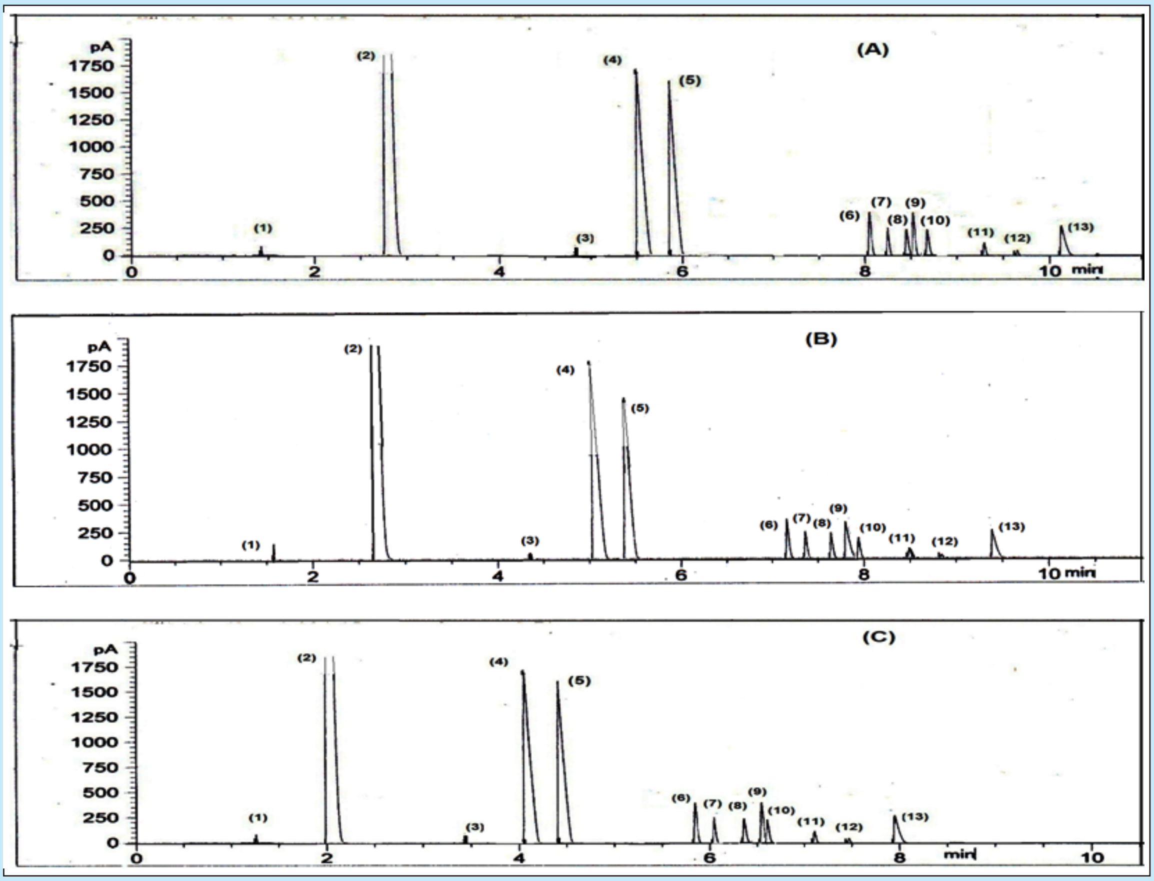

Figure 2
The effect of initial temperature of column on the GC separation of LPG standard using HP plot/Al_2O_3 column using temperature of (A) 25, (B) 35 and (C) 45°C Peak assignment: (1) ethane, (2) propane, (3) propylene , (4) iso-butane, (5) n-butane, (6) trans-2-butene, (7) 1-butene, (8) isobutylene, (9) neo-pentane, (10) cis-2-butene, (11) i-pentane, (12) n-pentane and (13) 1,3 butadiene

ethane> propane> propylene > iso-butane> n-butane > trans-2-butene > 1-butene > isobutylene, > neo-pentane > cis-2-butene > iso-pentane > n-pentane > 1,3 butadiene.

2. Effect of initial temperature

The effects of initial temperature (25, 35 and 45°C) were observed at flow rate of 5 mL min^{-1}. The retention times became progressively shorter as the initial temperature was increased (Figures 2a, b and c). In addition, all the peak were adequately resolved. Using the initial temperature 45°C (Figure 2C) shows that the retention time was found shortest compare with other initial temperature. However for the initial temperature above 45°C, the best retention time was found in the work by M. Feeney (2001). On the other hand, it was reported that higher initial temperature, for example above 45°C, might be reduce the separation time, it will need readjustment of flow rate to avoid peak overlapping.

A comparative study between the HP plot and OV-1 capillary columns for the separation of hydrocarbon in LPG and natural gas has been reported[10-11]. Previous study shows that OV-1 capillary column is less sensitive and the separation of every peaks were not satisfied, the elution time more than 30 min (Figure 3). In addition, the consistency and reproducibility of the OV-1 capillary column were much more difficult to be achieved compared to the HP Plot column, this is due to the OV-column used is based on particulate capillary materials. This material, are plagued by problem of backpressure. The use of this column resulted in good separations, but the separation time was longer (about 30 min) (Figure 3). From this study, the use of the HP Plot/Al_2O_3 column enables these analytes to be separated almost two times faster than OV capillary column and the final adopted for GC conditions were: gradient elution. The oven was set using temperature program from 30-50^{o}C, with ramp temperature at 10 ^{o}C min^{-1} and held for 5 min at 150^{o}C. Under these conditions, all the analytes were separated in less than 9 min (Figure 2B). The method readily lends itself as a useful analytical technique for the determination of LPG samples.

B. Analytical characteristics

The results of developed GC method were validated in terms of repeatability and reproducibility.

The repeatability of the peak area was assessed by injecting mixtures of standard (n=7). The reproducibility over different days was carried out by injecting the same standard solution over five days. The relative standard deviation (RSD) for some of LPG components were found propane (0,4497%), n-butane (0,8299%), iso-butane (0,2670%), n-pentane (1,9111%), iso-pentane (1,5218%), ethane (0,7607%), iso-butilene (0,5016%) and propylene (0,2734%), respectively.

C. Analysis of LPG Samples

In the analysis of LPG samples, peak identification was based on the comparison between the retention times of standard compounds and the sample of LPG. Quantification was based on the external standard method using calibration curves fitted by linear regression analysis. The analysis was performed in triplicate. The result of the analyzed samples is shown in Table 2.

LPG is composed primarily of propane and butane that produce from natural gas processing and petroleum refining. LPG samples (No.1 to 5) are type of LPG obtained exclusively from natural gas processing. It was observed that the content of samples are propane, butane as the main compounds and ethane, pentane as impurities.

Samples number 6-10 are type of LPG that produced from crude oil cracking at petroleum refineries. In petroleum refining, LPG is collected during distillation, from lighter compounds dissolved in the crude oil, as well as generated in the “cracking” of heavy hydrocarbons. Cracking is a process whereas large hydrocarbon molecules are broken down into smaller and more useful ones. LPG products that resulted by cracking activities will content the unsaturated hydrocarbon such as 1,3 butadiene, cis-2 butene, iso-butene, iso-butylene and neo pentane. When compared to Indonesian LPG specification, it can be seen that the composition of the LPG for all the analyzed samples have comply with the standards for each parameter (C_2<0.8 % mol, C_3+C_4>97 % mol and C_{5+}.<2.0 % mol).

IV. CONCLUSION

A rapid GC method using a HP Plot/Al_2O_3 column was developed, validated and applied to the simultaneous determination of LPG standard. The use of the HP Plot/Al_2O_3 column enables these analytes to be separated almost two times faster than OV capillary column. The method readily lends itself as a useful analytical technique for the determination of LPG samples. The relative standard deviation (RSD) for the LPG standard concentration were found to range between 0.27-1.91%.

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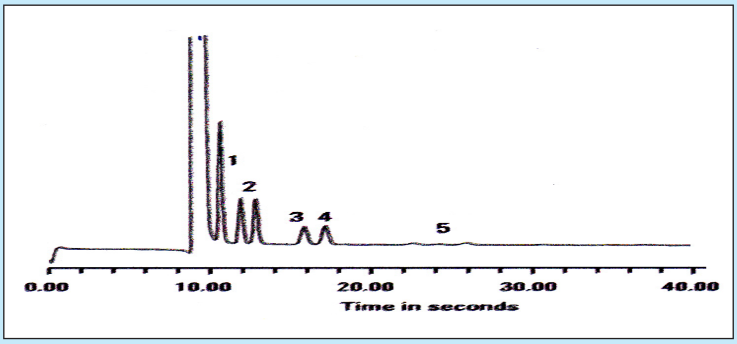

Figure 3
Separation of gas using a OV capillary column. Isocratic elution system with helium using a flow rate of 4 ml min^{-1}. Assignment of peaks : (1) i-butane,

Table 1
Analytical characteristics of the developed CG method

No	propane	n-butane	i-butane	n-Pentane	i-pentane	ethane	iso-butilene	propylene
1	59.0872	15.3789	15.6911	0.1989	0.5063	0.2004	0.9974	0.1005
2	58.7533	15.5426	15.6055	0.1991	0.5041	0.2008	1.003	0.1001
3	58.829	15.5021	15.5836	0.2039	0.508	0.2036	0.9996	0.1001
4	58.5538	15.6517	15.5886	0.2032	0.5194	0.2008	1.0065	0.0996
5	58.8932	15.4635	15.6038	0.1989	0.4946	0.2018	0.9997	0.1
6	58.9494	15.4323	15.6173	0.197	0.4999	0.2005	0.999	0.0999
7	58.3003	15.7471	15.6716	0.2079	0.5037	0.2041	1.0115	0.0999
Stdev	0.2643	0.1289	0.0417	0.0038	0.0077	0.0015	0.0050	0.0003
means	58.7666	15.5312	15.6231	0.2013	0.5051	0.2017	1.0024	0.1000
%RSD	0.4497	0.8299	0.2670	1.9111	1.5218	0.7607	0.5016	0.2734

Table 2
Levels of hydrocarbon contents in LPG samples

LPG Samples	Concentration (% mol)												
	ethane	propane	propylene	iso-C4	n-C4	1-butene	iso-butilen	cis-2-butene	trans-2-butene	Iso-C5	1,3 butadiene	n-C5	Neopentane
1	0.4756	55.2284	0.0000	16.2001	27.6420	0.0000	0.0000	0.0000	0.0000	0.3335	0.0000	0.0156	0.1048
3	0.1280	32.3615	0.0000	24.8921	41.8776	0.0000	0.0000	0.0000	0.0000	0.4918	0.0000	0.0000	0.2490
4	0.2433	61.5228	0.0000	12.3195	25.8074	0.0000	0.0000	0.0000	0.0000	0.0529	0.0000	0.0000	0.0540
5	0.2059	55.5139	0.0000	15.4844	28.5926	0.0000	0.0000	0.0000	0.0000	0.1053	0.0000	0.0000	0.0979
6	0.2931	36.3097	0.4577	19.8708	39.9471	1.2554	0.5444	0.2423	0.3758	0.3632	0.0142	0.1942	0.1324
7	0.3979	55.5538	0.4216	18.2373	23.4218	0.3611	0.4632	0.3046	0.5316	0.2009	0.0084	0.0097	0.0881
8	0.1628	32.8000	0.3724	28.0134	28.2514	2.4967	3.4271	1.4160	2.4161	0.3656	0.0081	0.0761	0.1184
9	0.2756	38.5168	0.9786	25.0163	20.1664	2.8580	3.8137	2.0833	3.5553	1.6394	0.0468	0.6734	0.0633
10	0.2121	26.7265	1.0454	34.5401	17.9219	4.5253	5.9365	3.1106	5.5325	0.3326	0.0328	0.0462	0.0375

REFERENCES

1. [14]**Andrew S. Brown, *et al*,** 2004, Analysis of natural gas by gas chromatography Reduction of correlated uncertainties by normalization, Journal of Chromatography A, 1040,
2. [17]**Andrew S. Brown,** 2004, Analysis of natural gas by gas chromatography: Reduction of correlated uncertainties by normalization, Journal of Chromatography A Volume 1040, Issue 2, 25 June.
3. [13]**Anwar Sutan, *et al.,*** 2003, Three Columns Gas Chromatograph Analysis Using Correlation between Component's Molecular Weight and Its Response Factor, Metco Services Ltd.
4. [5]**B. D Skrbic** and **M. J. Zlatkovic,** 1997, Simple Method for Rapid Analysisi of Natural Gas by Gas Chromatography, Chromatographia, Vol 17, No. 1, January.
5. [4]**Chris M. Wilkins**, 1998, Accurate LPG Analysis Begins With Sampling Procedure, Equipments, Oil and Gas Journal.
6. [6]**D2163-14,** 2000, Standard Test Method for Determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/Propene Mixtures by Gas Chromatography, reapproved.
7. [7]**D2712-91,** 2010, Standard Test Method for Hydrocarbon Traces in Propylene Concentrates By Gas Chromatography.
8. [8]**D5273-92,** 2012, Standard Guide for Analysis of Propylene Concentrates.
9. [9]**GPA 2166**, 2000, Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography, Gas Processor Association, Reapproved.
10. [10]**ISO 6974-5,** 2000, Natural gas – Determination of composition with defined uncertainty by gas chromatography – Part 5: Determination of nitrogen, carbon dioxide, and C1 to C5 and C6+ hydrocarbons for a laboratory and on-line process application using three columns.
11. [1]**Indonesian Energy Outlook,** 2012, BPPT.
12. [12]**Michael Feeney,** 2001, Micro GC Analysis of Natural Gas and LPG in Seconds Using the Agilent 300 Natural Gas Analyzer, Gas Chromatography, Agilent Technologies, USA.
13. [16]**Remko van Loon,** 2006, Mud Logging – Rapid Analyses of Well Gases with an Agilent Micro GC, Application Note, Agilent Technologies, Inc.
14. [2]**R. Nabavi, A. Niaei, D. Salari, J. Towfighi,** 2007, Modeling of thermal cracking of LPG: Application of artificial neural network in prediction of the main product yields, Journal of Analytical and Applied Pyrolysis, Volume 80, Issue 1, August.
15. [3]**Thomas Wenzel,** 2001, Separation Science - Chromatography Unit, Department of Chemistry, Bates College, Lewiston ME 04240.
16. [15]**Wang YH., *et al.,*** 2006, An improved gas chromatography for rapid measurement of CO_2, CH4 and N_2O, J Environ Sci (China). 18(1):162-9, 17.
17. [11]**Zhenghua Ji, Imogene Chang** and **Alan Broske**, 2000, Optimized Determination of C1-C6 Impurities in Propylene and Ethylene Using HP-Plot/$Al_2O_{3,}$ Agilen Technologies, Application note 228-263.