A RAPID GAS CHROMATOGRAPHY METHOD FOR SIMULTANEOUS DETERMINATION OF LPG COMPOUNDS

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ABSTRACT

A rapid gas chromatography method using a HP Plot/Al2O3 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/Al2O3 column

1. INTRODUCTION

LPG (Liquefied Petroleum Gas) as a fuel for household and industrial interests is 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 butylene 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\textsubscript{3}H\textsubscript{8}), butane (C\textsubscript{4}H\textsubscript{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 divinybenzene/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\textsubscript{2}O\textsubscript{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\textsuperscript{-1}, respectively. The temperature of the injector and detector was at 200 °C. The oven was set using temperature program from 30-50 °C, with ramp temperature at 10°C min\textsuperscript{-1} and held for 5 min at 150°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](image)

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.
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 peaks were adequately resolved. Using the initial temperature 45°C (Figure 2C) shows that the retention time was found shortest compared 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/Al₂O₃ 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°C, with ramp temperature at 10 °C min⁻¹ and held for 5 min at 150°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-butylene (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 (C₂<0.8 % mol, C₃+C₄>97 % mol and C₅<2.0 % mol).

IV. CONCLUSION

A rapid GC method using a HP Plot/Al₂O₃ column was developed, validated and applied to the simultaneous determination of LPG standard. The use of the HP Plot/Al₂O₃ 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

<table>
<thead>
<tr>
<th>No</th>
<th>propane</th>
<th>n-butane</th>
<th>i-butane</th>
<th>n-Pentane</th>
<th>i-pentane</th>
<th>ethane</th>
<th>iso-butilene</th>
<th>propylene</th>
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<td>0.1</td>
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<td>Stdev</td>
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<td>0.0015</td>
<td>0.0050</td>
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<tr>
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<td>15.6231</td>
<td>0.2013</td>
<td>0.5051</td>
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</tr>
<tr>
<td>%RSD</td>
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<td>0.8299</td>
<td>0.2670</td>
<td>1.9111</td>
<td>1.5218</td>
<td>0.7607</td>
<td>0.5016</td>
<td>0.2734</td>
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### Table 2
#### Levels of hydrocarbon contents in LPG samples

<table>
<thead>
<tr>
<th>LPG Samples</th>
<th>Concentration (% mol)</th>
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<td></td>
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<tr>
<td>9</td>
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</tr>
<tr>
<td>10</td>
<td>0.2121</td>
</tr>
</tbody>
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REFERENCES


11. Indonesian Energy Outlook, 2012, BPPT.


