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SIMULTANEOUS MEASUREMENT OF SYN-GAS COMPONENT (H_2, CO_2, CH_4, AND CO) AS PRODUCT OF BIOMASS GASIFICATION BY USING VALIDATED GC-TCD METHOD

PENGUKURAN SECARA SIMULTAN KOMPONEN *SYN-GAS* (H_2, CO_2, CH_4, AND CO) HASIL GASIFIKASI BIOMASSA MENGGUNAKAN METODE GC-TCD TERVALIDASI

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ABSTRAK

Gasifikasi biomassa telah dikenal secara luas sebagai salah satu cara untuk menghasilkan syn-gas, yang merupakan salah satu alternatif pengganti bahan bakar fosil. Namun demikian, verifikasi komposisi syn-gas secara akurat membutuhkan suatu metoda yang handal dan tervalidasi untuk menentukan secara simultan kandungan H_2*,* CO_2*,* CH_4*, dan CO. Untuk memenuhi kebutuhan tersebut, yang merupakan tujuan dari studi ini, sebuah metoda GC-TCD untuk mengukur komponen* H_2*,* CO_2*,* CH_4*, and CO secara simultan dalam syn-gas telah divalidasi sesuai dengan ISO/IEC 17025. Untuk mencapai tujuan dari validasi metoda tersebut, seluruh parameter kinerja metoda telah dievaluasi dan didiskusikan secara rinci. Hasil menunjukkan bahwa presisi intraday dan presisi interday dari metoda yang divalidasi dinyatakan dapat diterima, dengan %RSD yang lebih rendah dari 0.67 CV-Horwitz untuk presisi intraday dan lebih rendah dari 1.0 CV-Horwitz untuk presisi interday. Nilai bias dari metoda yang digunakan berada dalam kisaran* $\pm 2\sigma$ *untuk seluruh komponen syn-gas, yang mengindikasikan bahwa metoda yang digunakan adalah akurat. Koefisien korelasi* (R^2) *untuk seluruh komponen mempunyai nilai yang lebih lebih tinggi dari 0.99, yang menunjukkan bahwa metoda ini memiliki linearitas yang cukup baik. Adapun LoD dan LoQ untuk tiap komponen syn-gas menunjukkan nilai yang lebih rendah dari kisaran konsentrasi syn-gas pada umumnya. Ketahanan metoda yang divalidasi juga dapat diterima yang diindikasikan oleh nilai p-values yang lebih tinggi dari 0.05 untuk seluruh komponen syn-gas. Aplikasi metoda yang sudah tervalidasi untuk pengukuran komponen syn-gas terhadap contoh aktual menunjukkan bahwa metode ini dapat diandalkan dan mampu menghasilkan data yang akurat sehingga dapat dipergunakan dalam analisa rutin. Inovasi dari studi ini, sebagaimana ditunjukkan oleh hasil eksperimen, adalah untuk mengevaluasi performa dari metoda tervalidasi untuk penentuan konsentrasi komponen syn-gas secara simultan dalam satu channel, dibandingkan dengan metode yang telah diketahui secara umum dimana komponen-komponen syn-gas diukur secara terpisah dalam channel yang berbeda.*

Kata Kunci: *syn-gas*, GC-TCD, validasi metode.

ABSTRACT

Biomass gasification has been widely known method to produce syn-gases, which can be considered as great alternative substitution for fossil fuels. However, accurate verification of the syn-gas composition requires a reliable and validated method for simultaneous measurement of H_2, CO_2, CH_4, and CO. In order to fulfill the aforementioned requirements, which is the objective of this study; a GC-TCD method for simultaneous measurement of H_2, CO_2, CH_4, and CO component in syn-gas has been validated in accordance to ISO/IEC 17025 and its application for real samples. For the method validation purpose, all of the performance parameters were evaluated and discussed in detail in this study. Intraday precision and interday precision were found to be acceptable having the %RSD below 0.67xCV Horwitz and below 1.0xCV Horwitz, respectively. The bias value falls within $\pm 2\sigma$ for entire components, indicating that the method accuracy can be accepted. Coefficient correlation for all components was higher than 0.99, which means that the method has sufficient linearity. LoD and LoQ for each component were found to be lower than typical syn-gas concentration range. The method roughness was also found in an acceptable level (the *p*-values was higher than 0.05 for allctarget components. Application of the validated method for the measurement of a real syn-gas samples indicated that the method is quite reliable to produce an accurate data and the validated methid can be used in a routine analysis. The innovation of this study, as shown by experiment results, is to evaluate the validated method's performance for simultaneous determination of syn-gas components' concentration in one channel, compared to common method in which the syn-gas components were measured separatedly in a different channel.

Keywords: syn-gas, GC-TCD, method validation.

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I. INTRODUCTION

Rapid increase in global consumption of fossil fuels to meet energy demand might leads to a future challenge, which is depletion. It is commonly known that resources will eventually be depleted if extraction rate is faster than replenishment rate (Höök & Tang 2013). Some alternative resources were reported to carry the potential to replace fossil fuels, such as bioethanol (Thangavelu, Ahmed & Ani 2016), compressed natural gas, and liquid petroleum gas (Bielaczyc et al. 2015). Among other alternative energy sources, Biomass-originated fuels, known as biofuels, are known to be inexpensive and generate significantly less greenhouse gas emission than fossil-based fuels (Wang et al. 2014).

Biomass can be considered as renewable materials which contain some quantities of hydrogen, oxygen, and carbon. In order to produce biomass-based fuels, direct gasification process can be used as reported in previous study. It involves a reaction between materials (biomass in this case) and oxygen, air, or steam to produce syn-gas, which is usually combusted to produce electricity or heat (Huber, Iborra & Corma 2006). This process was known to be typically able to generate a gaseous mixture of H_2, CO_2, CH_4, and CO in percentage (%mol/mol) level (Dalai et al. 2003).

However, to accurately verify the composition of syn-gas such as H_2, CO_2, CH_4, and CO from a gasification process, a reliable method for simultaneous measurement of syn-gas components detection is extremely required. One method that has been widely known to be suitable for such applicationis the gas chromatography (GC), equipped with a thermal conductivity detector (TCD) (Zuas & Mulyana 2017).

Previous experiments has proven the capability of the TCD as a universal detector to measure permanent gases at %mol/mol level (Teodoru et al. 2015, Zuas et al. 2018) and it would likely be suitable for the concentration range of sawdust gasification products. For the GC-TCD system, both Porapak Q and Molsieve 5A might be used as the columns to separate H_2, CO_2, CH_4, and CO from their mixture (Zuas & Mulyana 2017), giving a posibble way for the measurement of such components in their mixture.

Some methods have been reported in previous articles for determination of syn-gas components, specifically using mass spectrometry (Weiland et al.

2014) and gas chromatography (Monarca et al. 2012), although without complete validation data. Another research article has reported the validation data for measurement of syn-gas components H_2, CO_2, CH_4, and CO using GC with dual TCD (Drolc, Djinovic & Pintar 2013). However, in the mentioned article, H_2 were determined separately in different channel from other components, therefore two TCD's were needed. Therefore, the objective of this study is to evaluate the method's performance for simultaneous measurement of the four syn-gas main components, supported by innovative idea of utilizing dual-packed column Porapak Q and Molsieve 5A as described in the next section. This method was expected to provide good separations and simultaneous detection of syn-gas components H2, CO_2, CH_4, and CO in one channel using only one TCD.

With the purpose to achieve a reliable measurement data, the performance of measurement method needs to be validated before use as recommended by ISO/IEC 17025 (International Organization for Standardization 2017). In this study, validation of GC-TCD method for a simultaneous measurement of H_2, CO_2, CH_4, and CO in their mixture was conducted and and the result are discussed.e, which might benefit for determination of sawdust gasification or other processes with similar product compositions. The validated method was then applied to measure the components in the syn-gas from the sawdust gasification process.

II. METHODOLOGY

A. Materials

For the method validation study, two sets of standard gas mixtures (SGMs), labeled as SGM-1 and SGM-2, were prepared gravimetrically. The preparation was based on ISO 6142, as an internationally accepted primary method for preparation of highly accurate standard gases (International Organization for Standardization 2002). According to ISO 6142, the gravimetric value of the gas mixtures was used instead of GC value (Budiman, Mulyana, & Zuas 2017). SGM-1 was utilized as the sample for all experiment conducted in the validation, while SGM-2 was used to assess the bias of the method. The concentration composition of both SGMs can be seen in Table 1.

Moreover, for the application study of the validated method, three actual syn-gas samples containing H_2, CO_2, CH_4, and CO were collected from the outlet of a sawdust gasification reactor. The samples were labeled as SGS-1, SGS-2, and SGS-3. All samples were measured using GC-TCD under the same procedure as in the validation study. The SGM-1 was used as the reference material to determine the concentration of the target components in all gasification samples.

Table 1
Gravimetric composition of the standard gas mixtures

Gas Components	Concentration (%mol/mol)	
	SGM-1	SGM-2
H_2	6.512	1.736
CO_2	15.575	4.144
CH_4	3.949	1.051
CO	8.938	2.378
He	matrix	matrix
Relative uncertainty of the concentration	1.25% (k=2)	

B. Instrument

An Agilent 7890B gas chromatography system equipped with thermal conductivity detector (GC-TCD) (Agilent Technologies, USA) was used for the simultaneous measurement of H_2, CO_2, CH_4, and CO concentration (Zuas, Budiman & Hamim 2017). To separate each component from their mixture, the GC was equipped with a 9 feet x 1/8 inch x 2.0 mm SS Molecular Sieve 5A packed column, (Restek, USA) connected in series with a 6 feet x 1/8 inch x 2.0 mm SS Porapak Q packed column (Restek, USA). The GC-TCD condition was firstly optimized to produce a reliable measurement result and obtained condition as seen in Table 2. In addition, a CMK calibrator (MCZ Umwelttechnick, Germany) was utilized for the dilution of the SGM-1 to obtain the calibration curve (Zuas et al., 2018).

C. Procedure

Based on ISO/IEC 17025 requirements, all method validation parameters were assessed under an optimized GC-TCD condition by adopting a procedure in previous validation study, consisting of identity confirmation, intraday precision and interday precision, accuracy, linearity, limit of detection (LoD), limit of quantification (LoQ), and roughness (Zuas et al. 2018). The validated method was then applied in the measurement of three syn-gas samples.

Table 2
Optimized operating conditions of the GC-TCD.

Apparatus	Conditions*
Injection	5 mL syringe for SGS injections; 100 mL/min via mass flow controller Brooks 0254 (Brooks Instrument, USA)
Sample loop	2 mL, stainless steel
Valve box temperature	100°C
Oven/Column temperature	Temperature programmed, 40°C (10 min), ramp up 60°C/min, 160°C (1 min)
Running time	13 min
Gas carrier	Helium ultra-high purity grade (99.999%) (Air Liquide, Singapore)
Carrier gas flow rate	28 mL/min
Detector temperature	250°C
Reference flow (He)	20 mL/min
Make up flow (He)	7 mL/min

*all of the optimized conditions in this table referred to previous experiment (Zuas et al. 2018).

For identity confirmation, the retention time and selectivity of detector response were observed and verified for each target component. The confirmation was firstly done to identify each component's peak in the chromatogram, before quantitative analysis can be conducted (Budiman & Zuas 2015).

Intraday precision of the method was observed by seven times injecting the SGM-1 under optimized GC-TCD, while interday precision was observed using the same procedure in different days (Zuas, Budiman & Hamim 2017). The percentage of relative standard deviation (%RSD) obtained from the repetitions was then compared with the coefficient of variance (CV) Horwitz. The CV Horwitz was calculated using Equation 1 (Zuas et al. 2018):

$$CV_{Horwitz} = 2^{1-0.5log^{c}} \quad (1)$$

The accuracy of the method was observed by measuring SGM-2 using the same procedure as in the precision. The peak area of the SGM-2's chromatogram was compared with SGM-1's to determine the measured value of target components in the SGM-1's. The difference between the gravimetric concentrations of each component (See Table 1) and the measured values were then calculated in order to determine bias of the method (Zuas, Budiman & Hamim 2017). This bias value can be compared with the method uncertainty, which was combined from standard deviation and the SGM's certified uncertainty (Budiman & Zuas 2015).

For the linearity, SGM-1 was dynamically diluted to seven point of concentration and injected to the GC-TCD under optimized condition by using the same procedure as in intraday precision. This was done to obtain the calibration curve and correlation coefficient (R^2) which is required for assessing of method linearity (Zuas, Budiman & Hamim 2017). Moreover, the chromatogram resulted from the injection of SGM-1's dilution with the lowest concentration point was also used to determine LoD and LoQ of the method. The LoD was calculated as three times of the signal to noise ratio (S/N ratio), while LoQ as ten times of the S/N ratio (Budiman & Zuas 2015).

The last validation parameter is method roughness, which was determined by slightly altering the GC-TCD operating conditions, including carrier gas flow rate, oven temperature, and detector temperature. Difference of the measurement results due to the change of the operating conditions was evaluated statistically using one-way ANOVA method to obtain p-values, in order to determine the significance effect of the parameter alteration (Magnusson & Örnemark 2014).

After all of the parameters were validated, the method was applied for measuring the syn-gas samples under optimized GC-TCD conditions. The

SGM-1 was used as the reference to determine the concentration of each target components in the syn-gas samples. The procedure for the syn-gas samples injection was the same as in the method validation study.

III. RESULTS AND DISCUSSION

A. Identity Confirmation

Identity of each component's peak in SGM-1's chromatogram (Figure 1), were confirmed through the properties of the obtained chromatogram such as retention times and selectivity factor. These parameters should be verified clearly before every target components in the mixture can be quantified (Budiman & Zuas 2015). It can be seen at Figure 1 that each component's peak of H_2, CO, CH_4, and CO_2 can be clearly distinguished from each other without any interference.

Selectivity factors (α) between each corresponding component were found to be higher than 1.0 and retention times were clearly differt from eacht. A selectivity factor (α) value higher than 1.0 is required for a good component separation indicator (Wenzel 2012). Therefore, the results in Table 3 indicated that each component in the sample mixture was distinctively separated from each other.

B. Intraday Precision and Interday Precision

Repeated SGM-1 injections of the sample have been done in one day to determine the method's intraday precision, and in different days for the method's interday precision. The %RSD values was calculated for each seven set of repetition, and compared to the CV Horwitz values corresponding to every target components. The %RSD values of SGM-1 injections can be seen in Table 4, along with their CV Horwitz values.

Based on analytical principle, the intraday precision of the GC-TCD method in this study can

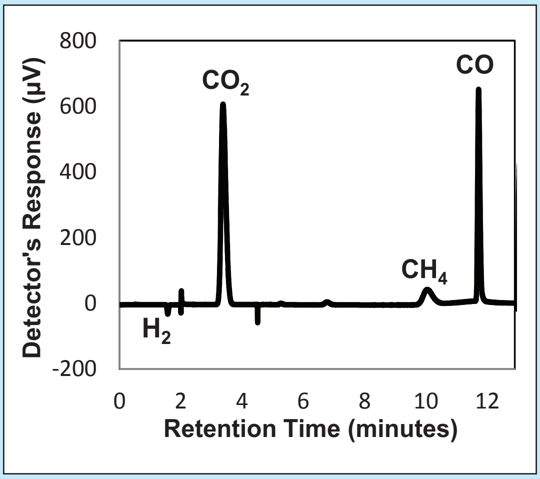

Figure 1
Typical chromatogram of components in standard gas mixture, obtained using GC-TCD with optimum operating condition shown in Table 2.

Table 3
Identity confirmation of H_2, CO, CH_4, and CO_2 peaks in the component

Gas Component	Parameter	
	Retention tim (t_R, min)	Selectivity factor (α)*
H_2	1.590	
		2.172
CO_2	3.455	
		3.023
CH_4	10.444	
		1.149
CO	12.005	

[*] selectivity factor values was calculated between two component peaks with closest retention times.

Table 4
%RSD and CV-Horwitz from repeated injections

Gas Comp.	Intraday %RSD	Interday %RSD	CVH* (%)	0.67 CVH* (%)
H_2	0.289	0.633	3.015	2.020
CO_2	0.202	0.484	2.645	1.772
CH_4	0.271	1.869	3.221	2.158
CO	0.250	1.225	2.876	1.923

[*] CVH = CV Horwitz

be considered acceptable since the %RSD values for every component in one day was found to be lower than 0.67 times of their corresponding CV Horwitz values (Zuas et al. 2018). These results were found to be comparable with previous experiment reported for the measurement of H_2, CO, CH_4, or CO_2 (Li & Guan 2009). In addition, there was a method reported in previous experiment showed a better precision, which is 0.07 %RSD for single target CO_2 measurement (Budiman & Zuas 2015). However, the intraday precision difference was compensated by the simultaneous multi-component measurement capability of the optimized method in this study.

Similar rule as in the intraday precision assessment can be applied for the observation of interday precision. But instead of 0.67 times CV Horwitz, the %RSD in different days was compared to 2.0 times of CV Horwitz value. Table 4 shows that %RSD values in different days for every target component were found to be lower than their corresponding CV Horwitz, hence the interday precision can be considered as acceptable (Zuas et al. 2018).

C. Accuracy

For the accuracy of the method, SGM-2 was injected into the GC-TCD using the same procedure as in SGM-1 injection. The bias value (σ) was calculated as the difference between the gravimetric concentration and the measured concentration resulted from the injection (Magnusson & Örnemark 2014)a number of important developments in analytical quality have taken place. Firstly, the ISO 9000 series of standards, which is widely used to provide a basis for a quality management system, has been revised. Its philosophy forms an integral part of international conformity assessment standards and guides, which underpins competence requirements for laboratories, proficiency testing (PT. To determine the accuracy of the GC-TCD method, the bias was compared to the expanded uncertainty of the method ($\pm$ 2σ) (Budiman & Zuas 2015), using equation (2) below (Zuas et al. 2018).

$$-2\,\sigma < \Delta C < 2\,\sigma \qquad (2)$$

σ values are the expanded uncertainty of the method, which can be estimated as following:

$$\sigma = \sqrt{S_b^2 + \frac{S_w^2}{n} + \mu_{RM}^2} \qquad (3)$$

in which S_b represents the standard deviation from intraday precision, S_w represents the standard deviation from interday precision, and ${}_{RM}$ represents the uncertainty of the SGM concentration (Budiman & Zuas 2015).

Bias value for each target component in the mixture was found to be within $\pm$2σ, as shown in Table 5. This result indicated that the measurement method had no bias (Zuas et al. 2018). Therefore, the accuracy of GC-TCD method under this study can be considered as acceptable.

D. Roughness

Alteration of GC-TCD's operating conditions were done for three parameters. For each parameter, two sets of different variable were evaluated by injecting SGM-1 using similar procedures as in the intraday precision assessment. Results for these measurements were statistically evaluated using one-way ANOVA method to obtain *p*-values for each parameter alteration (National Association of Testing Authorities 2013).

Table 5
Accuracy data of the GC-TCD method for H_2, CO_2, CH_4, CO measurement

Parameters	H_2	CO_2	CH_4	CO
Bias (% mol/mol)	0.036	0.046	0.269	0.015
Combined uncertainty, σ (% mol/mol)	0.091	0.124	0.234	0.143
$\pm$ 2σ (% mol/mol)	0.182	0.249	0.469	0.285

Table 6
One-way ANOVA evaluation results

Condition	*p*-values			
	H_2	CO_2	CH_4	CO
Flow rate				
- 26 mL/min	0.245	0.398	0.529	0.252
- 28 mL/min*				
- 30 mL/min	0.270	0.244	0.141	0.403
Oven temperature				
- 38ºC (10 min), ramp 58ºC/min, 158ºC (1 min)	0.382	0.461	0.286	0.181
- 40ºC (10 min), ramp 60ºC/min, 200ºC (1 min)*				
- 42ºC (10 min), ramp 62ºC/min, 202ºC (1 min)	0.300	0.439	0.336	0.127
Detector temperature				
- 248ºC	0.506	0.214	0.469	0.146
- 250ºC*				
- 252ºC	0.218	0.485	0.161	0.089

*optimum parameter condition

Table 7
Linearity data of the method for each component and their LoD and LoQ values

Gas component	Slope	Intercept	Linear range (% mol/mol)	n	R^2	LoD (µmol/mol)	LoQ (µmol/mol)
H_2	16.660	-1.644	0.300-6.512	8	0.99959	303.567	1011.890
CO_2	462.138	-133.600	0.719-15.575	8	0.99932	38.522	128.407
CH_4	280.579	-48.723	0.182-3.949	8	0.99564	182.316	607.721
CO	392.934	-43.669	0.413-8.938	8	0.99965	24.918	83.059

Previous experiment reported a confidence limit above 95% (which means *p*-value < 0.05) to indicate a significant effect of parameter alteration to measurement results (Budiman & Zuas 2015). In this study, *p*-values for every change of parameter were found to be above 0.05, as shown in Table 6. Based on these results, slight changes in operating conditions did not seem to have a significant effect the measurement results. Therefore, the method roughness was considered as acceptable.

E. Linearity, LoD and LoQ

Seven points concentration from SGM-1's was injected into the GC-TCD and the calibration curve was constructed. Coefficient correlation (R^2) for each target component was calculated from their linear regression range. In addition, the chromatogram from the lowest concentration injection was used to determine LoD and LoQ of the method using the signal to noise ratio.

As shown in Table 7, correlation coefficient values in the linear range for entire target components were found to be higher than 0.99. These values fall above the acceptance limit for linearity of analytical methods, as reported in other validation experiments (Chaursia et al. 2014).

Moreover, LoD and LoQ for each component were found to be significantly lower than the linear range. The LoD is the lowest concentration that can be detected by analytical methods while LoQ is the lowest concentration that can be accurately quantified (Magnusson & Örnemark 2014)a number of important developments in analytical quality have taken place. Firstly, the ISO 9000 series of standards, which is widely used to provide a basis for a quality management system, has been revised. Its philosophy forms an integral part of international conformity assessment standards and guides, which underpins competence requirements for laboratories, proficiency testing (PT, which means that the entire linear range was acceptable for sample quantification.

These results shown that the validated GC-TCD method in this study has suitable linear range to cover the typical concentration of syn-gas analysis. This was also supported by the fact that the LoD and LoQ of this method falls below the aforementioned concentration range. Therefore, the validated GC-TCD method in this study can be considered suitable for routine measurement of typical syn-gas concentrations.

F. Application for Actual Syn-Gas Samples

The validated method was applied to actual syn-gas samples analysis taken from sawdust combustion process. These samples were injected to the GC-TCD using similar procedure as in the precision evaluation.

The samples chromatogram was compared to the reference as shown in Figure 2, in which the identity of H_2, CO_2, CH_4, and CO can be verified based on each corresponding retention times. Concentration of each component (shown in Table 8) was quantified using the calibration curve of SGM-1 as the reference material.

It can be seen in Figure 2 that CH_4 and CO peaks of undiluted syn-gas chromatogram were higher than those of standard gas chromatogram. Therefore, syn-gas samples were diluted to fit the components' concentration in the calibration curve. However, sample dilution might contribute more to the uncertainty of the samples concentration (Milton, Vargha & Brown 2011). Aside of that, the %RSD of the measurement was relatively low, which fall for under 1.0 % for each target component in every syn-gas samples, as shown in Table 8 below.

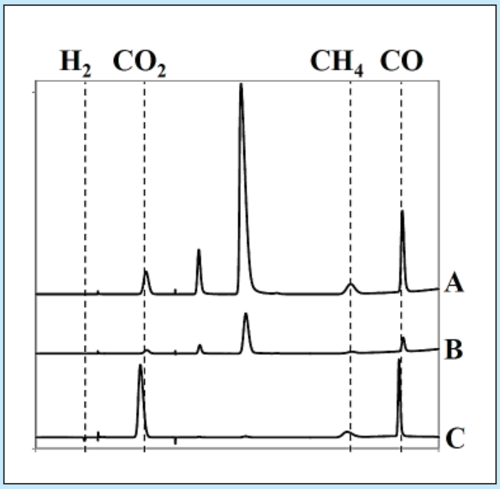

Figure 2
Comparison between typical chromatograms of; A (undiluted syn-gas sample), B (diluted syn-gas sample), and C (standard gas).

Table 8
Results of syn-gas samples measurement

Sample Code	Gas Comp.	Concentration (% mol/mol))	%RSD
SGS-1	H_2	0.044	0.441
	CO_2	4.310	0.301
	CH_4	3.545	0.672
	CO	10.909	0.887
SGS-2	H_2	n.d	-
	CO_2	4.157	0.330
	CH_4	0.332	0.942
	CO	4.888	0.307
SGS-3	H_2	0.181	0.872
	CO_2	5.810	0.330
	CH_4	6.115	0.368
	CO	12.514	0.549

IV. CONCLUSIONS

Based on the results discussed above, validated GC-TCD method in this study can be considered as a reliable method for routine measurement of H_2, CO, CH_4, and CO_2 in actual syn-gas samples.

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