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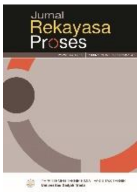

Analysis Method of Black Liquor Pyrolysis and Gasification Using Deconvolution Technique to Obtain the Real-Time Gas Production Profile

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ABSTRACT

In thermal reaction experiments, e.g., pyrolysis, combustion, and gasification, the gas released from the reaction can be analyzed in gas measuring instruments. There will be some time delay due to the relatively long gas travel from the reactor to the analyzers. Besides, there can be some time lag in the gas measuring instrument. Gas dispersion may furthermore occur and thus alter the gas concentration profile. The observed gas concentration, therefore, can be very different from the original gaseous reaction products profile. A mathematical procedure called deconvolution technique will be used to get the original gaseous reaction products concentrations profile. The deconvolution technique is based on the assumption that original data have been altered by a transfer function to yield observed data. By the deconvolution techniques, the transfer function for each data set will be calculated and then can be used to compute the original data. In this study, the deconvolution technique was applied to the concentration profile of gaseous products from black liquor pyrolysis and gasification reactions measured by gas analyzers instruments to obtain the real-time gas concentration profile during the processes. Tracer gases are injected in the reactor To facilitate the deconvolution calculation, and their concentration profiles observed in the measuring instruments are recorded. Gaseous products that are analyzed are CO_2, CO, CH_4, SO_2, and H_2S. This technique can successfully provide the real-time gas production concentration profile from the black liquor pyrolysis and gasification reaction.

Keywords: black liquor; deconvolution; gasification; pyrolysis; residence time distribution

ABSTRAK

Dalam reaksi termal seperti pirolisis, pembakaran, dan gasifikasi, gas hasil reaksi dapat dianalisis dengan instrumen analisis gas. Akan ada penundaan waktu deteksi karena waktu tempuh dari reaktor ke alat analisis. Ada juga tambahan waktu karena pemrosesan dalam instrumennya. Dispersi gas juga mungkin terjadi yang akan mengubah profil konsentrasi

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gas.Profil konsentrasi gas yang terdeteksi bisa jadi akan sangat berbeda dengan profil produksi gas yang sebenarnya. Untuk mendapatkan profil konsentrasi yang sebenarnya, dapat digunakan sebuah prosedur matematika yang disebut dekonvolusi. Dalam prosedur ini diasumsikan profil gas telah diubah oleh sebuaf fungsi transfer sehingga menghasilkan profil gas terboservasi. Dengan teknik dekonvolusi, fungsi transfer ini akan dicari sehingga bisa dipergunakan untuk menghitung profil gas sebenarnya. Dalam penelitian ini profil gas hasil reaksi pirolisis dan gasifikasi lindi hitam yang terdeteksi dalam instrumen analisis gas akan didekonvolusi untuk mendapatkan profil produksi gas yang sebenarnya. Untuk itu sebuah gas pendeteksi diijeksikan ke dalam reaktor dan profil konsentrasinya diukur dengan instrumen analisis. Gas yang dianalisis adalah CO_2, CO, CH_4, SO_2, and H_2S. Dengan teknik ini profil produksi gas yang sebenarnya dari reaksi pirolisis dan gasifikasi berhasil diperoleh.

Kata kunci: *dekonvolusi; distribusi waktu tinggal;lindi hitam;gasifikasi; pirolisis*

1. Introduction

Black liquor is the liquor product from the pulping process industry. It contains spent inorganic pulping chemicals mixed with dissolved organic material, mostly lignin, hemicellulose, and cellulose. The black liquor is conventionally used as the fuel in a Kraft recovery boiler in the pulping plant. The steam from the recovery boiler can be used as a process steam in the plant, and the excess can be used for power generation in a steam turbine. To further increase the efficiency of the heat and power generated from the black liquor, a gasification process is proposed. However, it is still under research and development.

The kinetics of black liquor pyrolysis, combustion, and gasification have been studied using several techniques. Two techniques commonly used are thermogravimetric analyzer (Li and van Heiningen, 1991; Li and Van Heiningen, 1990; Sánchez et al., 2004; Zhao et al., 2010) and fixed bed reactor experiment (Bhattacharya et al., 1986; Demirbaş, 2002). In the TGA experiments, only less than 10 mg of samples are needed. The mass changes of the black liquor droplet over the reaction time can be studied, and the gaseous products can be analyzed if the outflow gas is connected to gas analyzers. In the fixed bed reactor experiments, usually more samples are needed. The mass changes during reaction time cannot be studied, but the quantity of the gaseous products, and the tars from the pyrolysis reaction, can be measured over time. The gaseous concentration in the produced gas can also be analyzed as in the TGA experiments.

The gaseous product concentration measurements never perfectly quantify the real-time reaction behavior due to at least two causes: 1. error in the instruments (Haver, 2009); and 2. deviation from the ideal flow pattern in the reactor (Levenspiel, 1999). According to O'Haver (2009), there are two types of instrumental measurement errors: systematic error and random error. The systematic errors give measurement values lesser or greater than the real value by a fixed percentage. This type of error usually can be compensated by instrument calibration. In comparison, random errors give unpredictable variations in the measurement value. This random error is commonly called noise. There are many sources of noise, such as vibrations, electric voltage or current fluctuation, air currents, and many other factors. Figure 1 illustrated the behavior of the random noise in the measurement results. The noise is more complex to be canceled out, and it needs treatment with special signal processing techniques. Besides the instrument error, the non-ideality of the flow pattern in the reactor can also give deviation in the measurement. There are two ideal flow patterns in the reactor: plug flow and mixed flow (Levenspiel, 1999). According to Levenspiel (1999), the deviation from these ideal patterns can be caused by the residence time distribution (RTD), the stage of aggregation between phases, and the earliness or lateness of mixing.

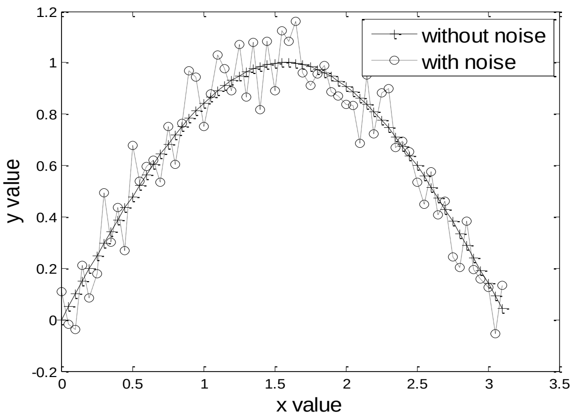


Figure 1. Comparison of measurement signal with and without noise.

The imperfection in the measured gas concentration in pyrolysis, combustion, or gasification reactions needs to be compensated to regain the real-time gaseous production over reaction time. Non-ideality of the flow pattern in the reactor will alter the gas concentration profile over time. Elements of flows may take a different route in a vessel; thus, each element has a different length of time to pass the vessel. The distribution of the time taken by the elements to leave the vessel is called exit age distribution (E) or residence time distribution (RTD) (Levenspiel, 1999). Mathematically, it is written as in Equation (1). The residence time distribution can be obtained experimentally by instantaneous injection of a tracer gas into the vessel and measuring the outflow gas concentration from the vessel. This procedure is illustrated in Figure 2.

$$\int_0^\infty E\,dt = 1 \tag{1}$$

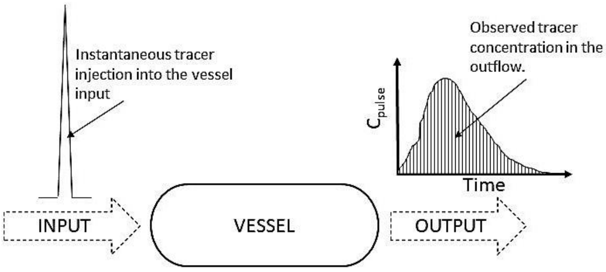


Figure 2. Residence time distribution experiment (redrawn from (Levenspiel, 1999))

Several researchers have conducted measurements and modeling of the RTD in various reactor systems. Serres et al. (2018) measured the RTD in a packed bed tubular reactor using impulse tracers. Then, the RTD was modeled using an empirical correlation. More recently, Wojewódka et al. (2019) conducted the RTD measurement in a spinning fluid reactor. In this experiment, the real RTD of the reactor was calculated from the detected output signals of the tracer using deconvolution techniques. The calculation result gave a good agreement with the experimental values, thus confirming the accuracy of the calculated RTD. In another study, Jafarikojour et al. (2014) presented the application of the RTD concept in the kinetics study of toluene photodegradation using a tubular reactor. Even though the reactor was tubular, the RTD measurements showed that continuous stirred tank reactors in series are a better description of the degradation kinetics in the study.

This study aims to develop a procedure to obtain the real-time gas concentration profile from pyrolysis and gasification reactions of black liquor. For kinetics study, the real-time concentration profile is essential. The gaseous product concentration leaving the reactor are measured using online gas analyzers. This concentration profiles are not representing the real-time gaseous production from the reactions due to the noises and non-ideality of the flow pattern, as discussed above. Digital signal processing techniques will be used for obtaining the real-time profile of the measured gas concentration.

2. Research Methodology

2.1 Materials

Concentrated black liquor from a softwood pulping process was used in this study. It was obtained from a pulp mill in Gothenburg, Sweden. The solid content in the concentrated black liquor was 66.0%. The black liquor had elemental compositions shown in Table 1.

Table 1. Elemental composition of black liquor for the study

Component	Black liquor used in single droplet TGA
Carbon, C	36.3
Hydrogen, H	3.1
Nitrogen, N	0.07
Sulfur, S	2.8
Chlorine, Cl	0.32
Sodium, Na	19.7
Potassium, K	2.44
Oxygen (by difference)	35.27

2.2 Procedures

The pyrolysis and gasification of black liquor involve many complex chemical reactions in addition to the physical processes. A specially built thermo-gravimetric analyzer (TGA) for a single droplet black liquor reaction has been constructed to study most of the phenomena that occur during pyrolysis and gasification.

2.2.1 Experimental setup

The TGA device holds three types of instruments: 1. gas flow controllers, to control the input gas to the TGA equipment; 2. gas heaters, to preheat gas input to the TGA to the desired temperature; 3. analyzing instruments that consist of the thermocouple to measure the temperature inside the droplet, an analytical balance to measure the droplet mass changes, a video recorder to visually observed the droplet behavior, and gas analyzers to measure the outflow gas concentration. The gas analyzers can measure the level of CO_2, CO, CH_4, SO_2, and H_2S. The general scheme of the TGA equipment can be seen in Figure 3.

During an experiment, a black liquor droplet with known mass was placed on the hook made by the thermocouple wire. The droplet diameter was adjusted to be about 2 or 3 mm. The TGA furnace was firstly preheated to the desired temperature. Then, the droplet on the hook was then inserted into the furnace. The temperature in the furnace can be set up to 900°C. For the pyrolysis experiments, nitrogen gas was used as the input gas, and for the gasification experiments, a mixture of carbon dioxide and nitrogen gas is used. The concentration of CO_2 is 2%.

Only the gas concentration profiles obtained by the gas analyzer were presented in this paper. As can be seen in Figure 3, the gaseous products from the droplet were carried by the carrier gas, leaving the furnace. The temperature of the gas was too high for the gas analyzer instrument; therefore, it needed to be cooled in the gas coolers. Then, the cooled gas entered the gas analyzers, and the concentration could be measured directly.

2.2.2 Mathematical model

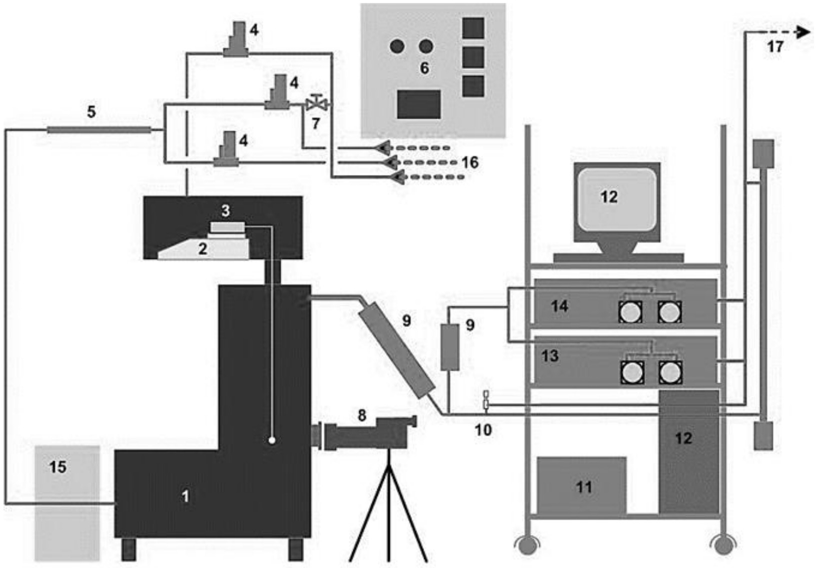
The quantity of tracer that was instantaneously injected into a vessel can be calculated by Equation (2).

$$a = \int_0^\infty f(t)\, dt \tag{2}$$

where *a* is the quantity of tracer, *f(t)* is the function describing residence time, and *t* is time. The residence time distribution function of the tracer will be given by Equation (3).

$$E = \frac{f(t)}{a} \tag{3}$$

The pulse signal of the tracer will be modified by the RTD to yield the observed signal. Thus if the RTD is known, the observed signal of the gas leaving the vessel can be calculated. This integration method is called convolution integral (Levenspiel, 1999). The derivation of convolution integral can be illustrated in Figure 4 (Levenspiel, 1999).



Legend:
1. Furnace
2. Balance
3. Thermocouple
4. Digital mass flow controller
5. Static mixer
6. Power regulator
7. Valve
8. Video camera
9. Gas cooler
10. Relief valve
11. Computer
12. H_2S analyzer
13. CO_2/CO analyzer
14. CH_4/SO_2 analyzer
15. Transformator
16. Gas sources
17. stack

Figure 3. General scheme of the TGA device

$$\begin{pmatrix} tracer\ leaving \\ in\ rectangle\ B \end{pmatrix} = \begin{pmatrix} all\ the\ tracer\ entering\ t'seconds\ earlier\ than\ t, \\ and\ staying\ for\ time\ t'in\ the\ vessel \end{pmatrix} \tag{4}$$

$$\begin{pmatrix} tracer\ leaving \\ in\ rectangle\ B \end{pmatrix} = \sum_{\substack{all\ rectangles \\ A\ which\ enter \\ earlier\ than \\ time\ t}} \begin{pmatrix} tracer\ in \\ rectangle \\ A \end{pmatrix} \begin{pmatrix} fractio\ of\ tracer\ in\ A \\ which\ stays\ for\ about \\ t'in\ the\ vessel \end{pmatrix} \tag{5}$$

$$C_{out}(t) = \int_0^t C_{in}(t-t')E(t')dt' \qquad (6)$$

$$C_{out} = E * C_{in} \qquad (7)$$

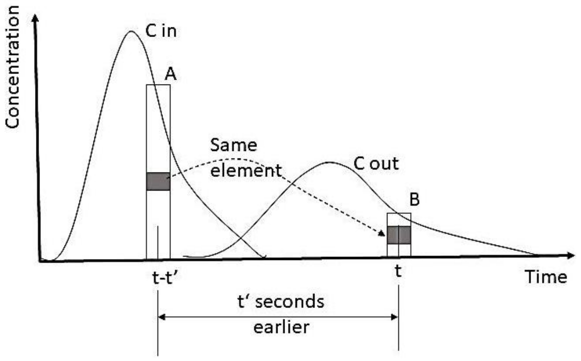


Figure 4. Derivation of convolution integral

Convolution in the time plane equals the multiplication in the frequency plane (Liliedahl et al., 1991). Equation (7) can be written using Fourier transform as in Equation (8).

$$\mathcal{F}[C_{out}] = \mathcal{F}[E] \cdot \mathcal{F}[C_{in}] \qquad (8)$$

In the case of the experiments, the known quantity is the observed outflow concentration (C_{out}) and the residence time distribution (E). The input concentration (C_{in}) can be calculated by re-arrangement of Equation (8) and taking the inverse Fourier transform. This procedure is called deconvolution and presented in Equation (9).

$$C_{in} = \mathcal{F}^{-1}\left[\frac{\mathcal{F}[C_{out}]}{\mathcal{F}[E]} \cdot\right] \qquad (9)$$

The deconvolution procedure is susceptible to the noise in the transfer function (E). Therefore, the calculated C_{in} needed to be filtered using a digital filter of the digital signal processing procedure. In this study, the filter that is used is the Butterworth filter. The detailed calculation procedure is described by Liliedahl et al. (1991). The calculation is performed using Octave software that is equipped with digital signal processing toolbox.

3. Results and Discussion

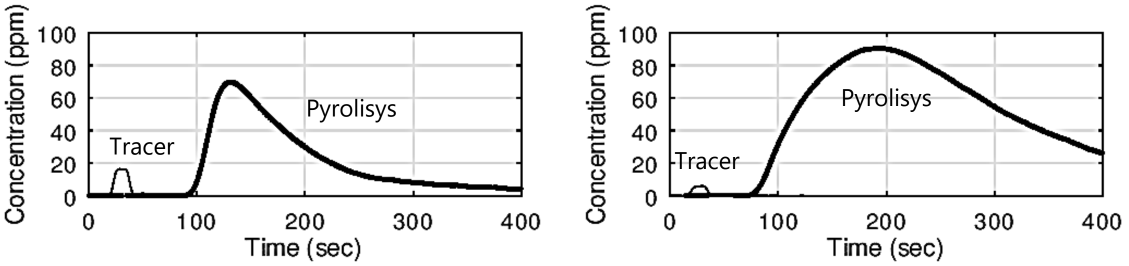
3.1 Experimental Data

The pyrolysis and gasification experiments were performed at a temperature of 900°C. In the pyrolysis experiment, nitrogen gas was used as the input gas. The nitrogen was inert gas to make sure that only pyrolysis or thermal decomposition of the material in the black liquor took place during the process. For the gasification experiment, a mixture of CO_2 gas and nitrogen was used. In general, the detected gas concentration profile had a similar shape with the other references (Jafarikojour et al., 2014; Serres et al., 2018; Wojewódka et al., 2019).

Figure 5 presents the gaseous products from the pyrolysis reaction at 900°C. All five tracer gases were detected in the analyzers. However, only four gases were identified during the pyrolysis experiment at 900°C. CO is the main gas products from the black liquor pyrolysis. CO_2 and CH_4 were also detected in significant amounts. However, SO_2 is only slightly detected, and the H_2S was not detected.

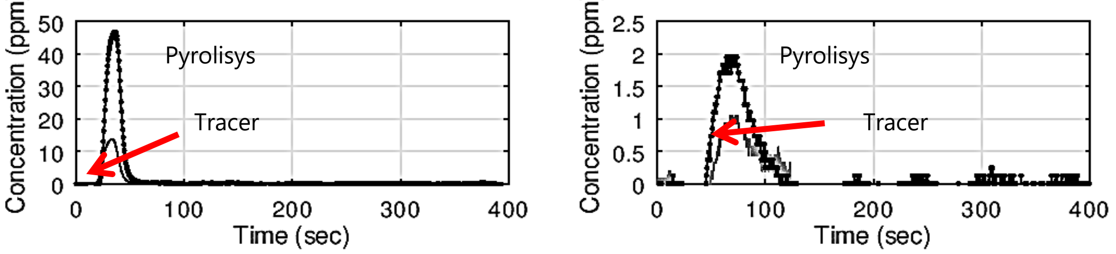
In the gasification process, the CO_2 reacted with the carbon in the black liquor according to Equation (10). The observed gas production is presented in Figure 6. Only two gaseous products were detected in the gasification products: CO and CH_4. Therefore, the tracer gases that were shown in the graph are also only for CO and CH_4.

$$C + CO_2 \overset{k}{\rightarrow} 2CO \qquad (10)$$



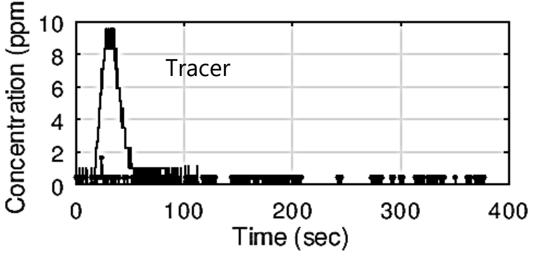
(a) CO_2 gas

(b) CO gas



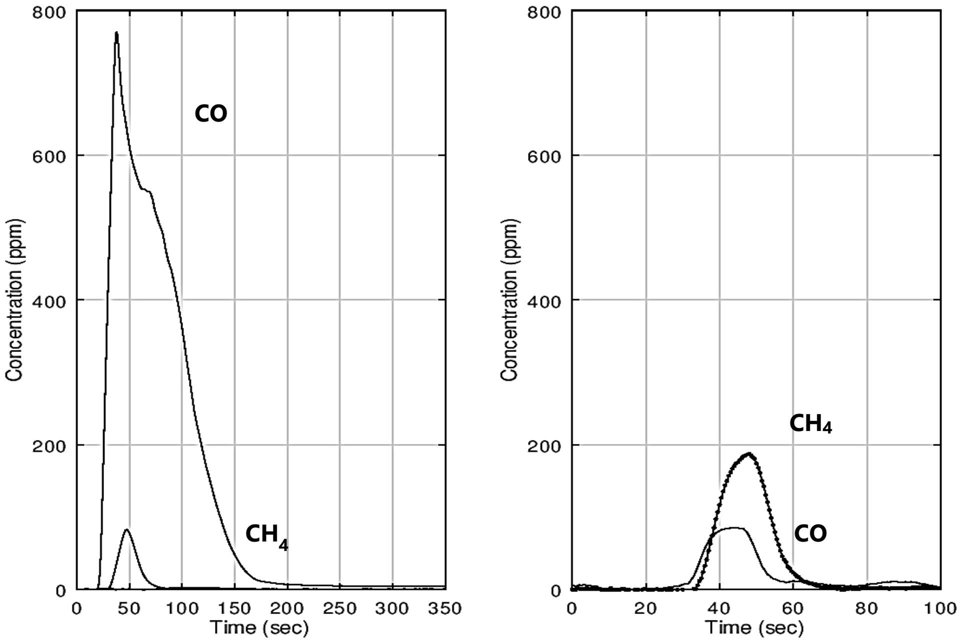
(c) CH_4 gas

(d) SO_2 gas



(e) H_2S gas

Figure 5. Measured gas concentration during pyrolysis reaction and the tracer gas: (a) CO_2 gas, (b) CO gas, (c) CH_4 gas, (d) SO_2 gas, and (e) H_2S gas



(a) Gasification products

(a) Tracer gases

Figure 6. Measured gas concentration during gasification process and the tracer gas: (a) gasification products and (b) Tracer gases.

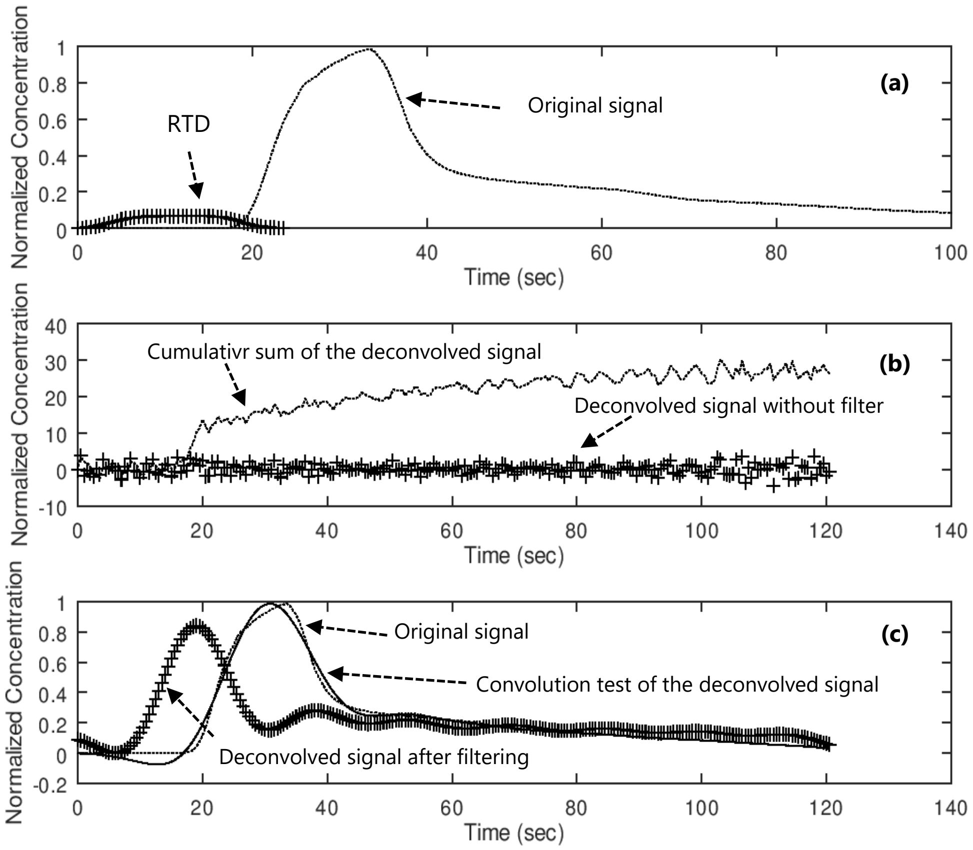


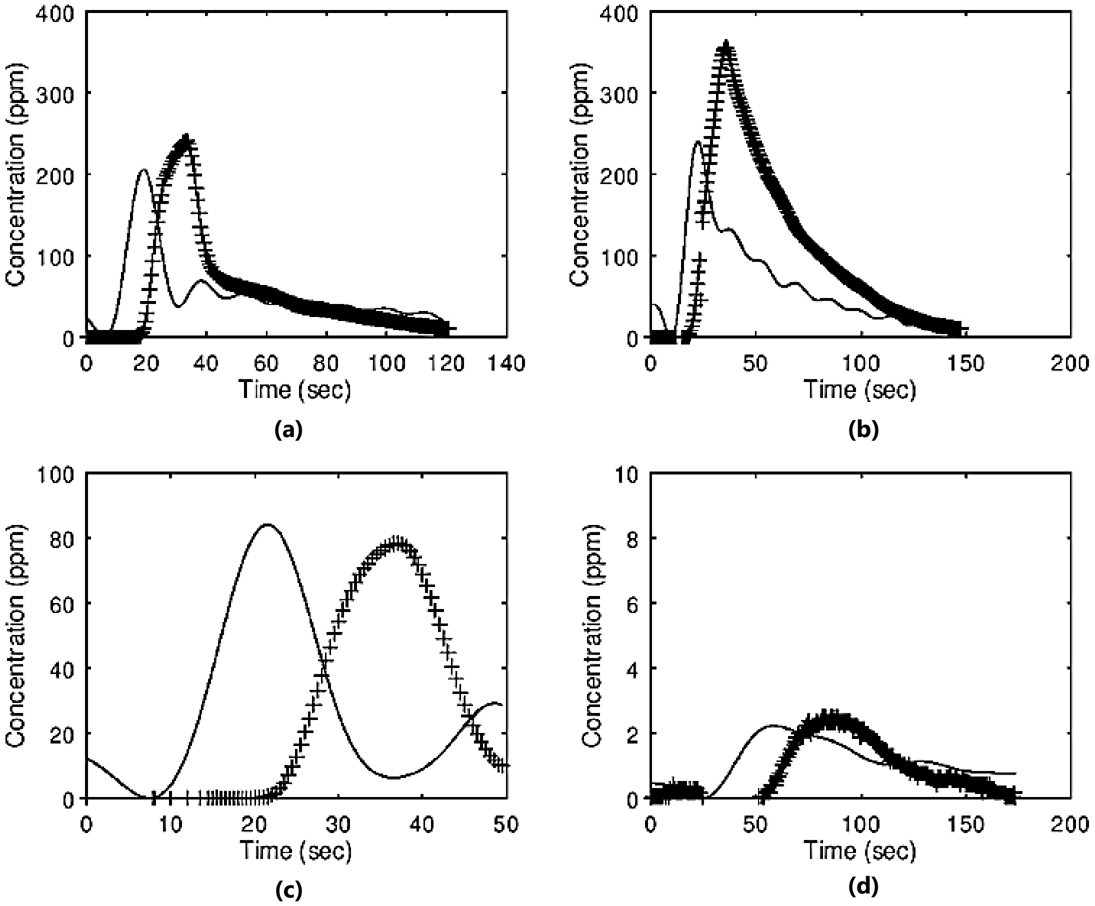
Figure 7. Deconvolution process for CO_2 gas from pyrolysis reaction at 900°C: (a) RTD and the normalized gas profile, (b) deconvolved signal and its cumulative sum, and (c) deconvolved signal after filtering

3.2 Deconvolution Process

The raw experimental data of gas production were deconvolved through sequential processes. At first, RTD was calculated from the tracer gas using Equation (2) and (3). Secondly, deconvolution was done by Fourier transform using Equation (9). Finally, the filtration by Butterworth digital filter was carried out in the Octave software signal processing toolbox. The sequences were illustrated in Figure 7 for the deconvolution of CO2 gas from the pyrolysis process at 900°C.

In Figure 7(a), the RTD was calculated by dividing the observed tracer gas profile by the total amount of the tracer gas. The original signal was also normalized or divided by the total amount of the tracer gas to make those two signals in the same order of magnitude. The normalized signals then deconvolved by the Fourier transform method as in the Equation (9). The result looked like a random signal due to heavy pollution by the noises. However, the cumulative sum of the message could be calculated and plotted in Figure 7(b). Figure 7(b) indicated the expected trend, i.e., the cumulative sum was increasing over time and relatively flat in the end. Therefore, there were some useful information could be obtained by filtering the seemingly random signal. The digital filter used was a Butterworth filter that was characterized by filter order and frequency cut off. It was assumed that the noises were mostly had high frequencies, so they could be canceled out by filtering the signal frequencies above the chosen cut off frequency. The order and cut off frequency was obtained by trial and error with the objective was to get the test signal, i.e., the convolution of the deconvolved signal as close to the original as possible. The result was presented in Figure 7(c). Some ripples still can be seen in the deconvolved signal. However, the trend of the real-time gas production profile can be seen from the plotted data.

Figure 8 shows the deconvolved data or the real-time data profile from the pyrolysis reaction, while Figure 9 presents the gasification reaction at 900°C. In general, the deconvolved data plots had the same shape with the measured data profile, even though they were shifted backward. The measured data also had a broader shape, which indicated a longer response time than the real reaction. The shape and behavior of the detected and the calculated information, however, displayed similarity with the results in the Jafarikojour et al. (2014) study. That study also identified that the detected data were consistently broader if compared with the real concentration calculated using deconvolution techniques. The aforementioned behaviors might be caused by the effect of gas dispersion and gas mixing inside the reactor and during the transportation to the gas analyzers.



(a)

(b)

(c)

(d)

Figure 8. Measured (+++) and real-time (---) gas production from pyrolysis reaction at 900°C: (a) CO_2 profile, (b) CO profile, (c) CH_4 profile, and (d) SO_2 profile

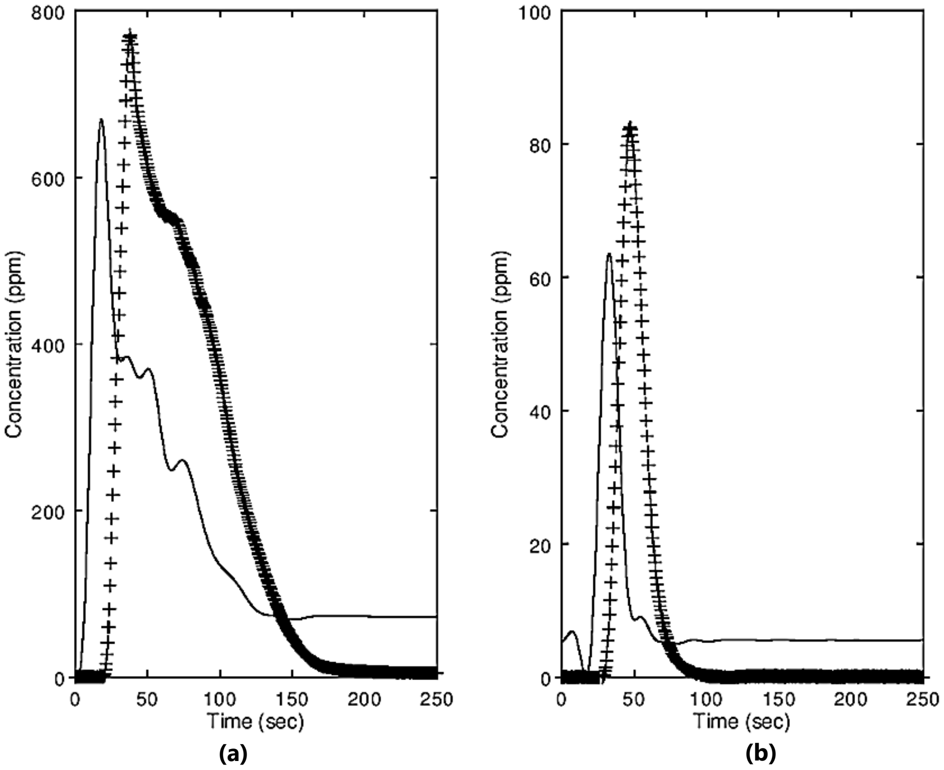


Figure 9. Measured (+++) and real-time (---) gas production from gasification reaction at 900°C: (a) CO_2 profile and (b) CH_4 profile

In all the deconvolved data, ripples can still be found in the profiles. These ripples indicated that not all of the noises could be filtered. A further study is needed to find the more suitable digital filter techniques that can be used to cancel out more noises to obtain a cleaner and more reliable real-time data profile.

4. Conclusions

The gas production profiles from black liquor pyrolysis and gasification reaction can be measured using the TGA instrument that has been built. The gas concentration profile can then be deconvolved to obtain real-time gas production. The deconvolution processes yield a heavily polluted signal that needs to be digitally filtered to get real-time data. In general, the real-time gas production profile can be obtained by the deconvolution procedure used in this study.

Acknowledgements

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Notation

a = quantity of tracer, mol
C_{in} = inflow gas concentration, ppm
C_{out} = outflow gas concentration, ppm
E = residence time distribution, -
$f(t)$ = transfer function, -
t = time, s

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