A THEORETICAL EQUATION PRESENTING SLOPE IN VAN KREVELEN DIAGRAM FOR BIOMASS PYROLYSIS

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ABSTRACT

The van Krevelen diagram has been used widely to describe the change of biomass composition during the thermochemical decomposition. However, the theoretical background on how the composition point of raw material moves towards the point of the product with thermochemical decomposition on the diagram has not been well clarified. This paper attempted to formulate a theoretical equation presenting the slope in van Krevelen diagram based on the removal rates of volatile products during thermochemical decomposition. An equation was established to predict the slope of the movement (or called as the reaction trend line) based on the generated amount of volatiles ($H_2O, CO_2, CO$ and organics) during thermochemical conversion. This equation was applied to predict some empirical trend lines for torrefaction to confirm the relevance of this equation, the consistency was excellent. Furthermore, the equation shows its capability in representing other thermal degradation process with a slope variation depending on the raw material.

Keywords: Biomass; thermochemical decomposition; van Krevelen diagram; change of composition.

INTRODUCTION

The van Krevelen diagram was created by Dirk Willem van Krevelen to assess the origin and maturity of kerogen and petroleum [1] as seen in Figure 1. Type I mainly has algal/sapropelic kerogen and is often associated with anoxic environments in lake sediments. Type II has lipid-rich kerogen from planktonic origin and mainly associated with marine sediments. Type III has humic kerogen derived from plant material. Most coals belong to type III source rocks [2].

Later on, the reaction trend lines were added to the diagram to indicate the structural relationships among families of compounds brought by reactions that involve the loss or gain of elements in a specific molar ratio as given in Figure 2. Lines from each reaction path have characteristic slopes or interceptions that can be easily demonstrated based on mathematical calculations [3]. From these lines, the possible product can be determined visually from various reactions. The equation represented by these lines is given as in Equation 1 where $H, O, C$ is the mole of hydrogen, oxygen, and carbon in the material.

$$\frac{H}{C} = -a\left(\frac{O}{C}\right) + b$$

(1)

The trend line represents dehydration/condensation have a slope of -2 $(a = 2)$. Hydrogenation / dehydrogenation is a vertical line. However, this equation is difficult to present the line for demethanation/methanation or decarboxylation/ carboxylation due to the variation of the slope of the equation for the reaction of one group.
In 1964, Tang utilized van Krevelen diagram for discussing the pyrolysis of cellulose fiber [5]. Torrefaction has been known as a biomass upgrading method since 1980s [6], [7]. In an ECN report, Bergman firstly used the van Krevelen diagram for biomass torrefaction [8] to provide insights on the differences in elemental composition of various (torrefied) wood and peat samples. The relative loss of oxygen and hydrogen compared to carbon that was taken in consideration for the discussion of the relationship with calorific value, and so forth.
Since then many reports have used this diagram to
discuss thermochemical decomposition of biomass,
including pyrolysis [9–12], dry torrefaction [13–16],
wt torrefaction (hydrothermal torrefaction) [17–
20], and hydrothermal treatment [21–23]. The slope
of trajectory of the moving data points during the
decomposition have been reported, and it is related
to the change in ratio of hydrogen, oxygen, and
carbon presented as decarboxylation or dehydration
trend line.

However, the theoretical background of this trend
has not been proposed. In this paper, the authors
attempted to formulate a theoretical equation
presenting the slope in van Krevelen diagram.

MODEL DEVELOPMENT

The transformation of the raw material (point 1) to
decomposed product (point 2) is presented in Figure 3.

The slope of this trend line is calculated by taking the
fraction of \( \frac{d(H)}{C} \) over \( \frac{d(O)}{C} \) and it can be expressed in
van Krevelen diagram by Eqs. 2 – 3.

\[
\frac{d(O)}{C} = C \frac{dO}{dt} \frac{dC}{dt}
\]  \( 2 \)

\[
\frac{d(H)}{C} = C \frac{dH}{dt} - \frac{dC}{dt}
\]  \( 3 \)

where \( \frac{d(H)}{C} \) and \( \frac{d(O)}{C} \) are the deviation of H/C and O/C
mole fraction when the material transformed from
raw material (point 1) to the decomposed product
(point 2).

A slope in van Krevelen diagram is expressed by
dividing Equation 3 by Equation 2:

\[
Slope = \frac{\frac{d(H)}{C}}{\frac{d(O)}{C}} = \frac{C \frac{dH}{dt} - \frac{dC}{dt} \frac{dH}{dt} - \frac{dC}{dt}}{C \frac{dO}{dt} - \frac{dC}{dt} \frac{dO}{dt} - \frac{dC}{dt}}
\]  \( 4 \)

**Figure 3** Presentation of a reaction trend line and its slope as the material transform from
point 1 to point 2 after the reaction. Point 1 is raw material (initial point) and point 2
is decomposed product (end point after the reaction).
where \(-dH/dt\), \(-dC/dt\), and \(-dO/dt\) are the deviation of mole hydrogen, carbon, and oxygen during the reaction process at any time \(t\).

The three derivative terms, \(-dH/dt\), \(-dC/dt\), and \(-dO/dt\), can be expressed by Equations 5 – 7 under the assumption that the volatile products are water (H\(_2\)O), carbon monoxide (CO), carbon (CO\(_2\)), and organics (C\(_a\)H\(_b\)O\(_γ\)).

\[
-\frac{dH}{dt} = 2\frac{dH_2O}{dt} + \beta \frac{dC_aH_bO_\gamma}{dt} \\
-\frac{dC}{dt} = \frac{dCO}{dt} + \frac{dCO_2}{dt} + \alpha \frac{dC_aH_bO_\gamma}{dt} \\
-\frac{dO}{dt} = \frac{dH_2O}{dt} + 2\frac{dCO}{dt} + \frac{dCO_2}{dt} + \gamma \frac{dC_aH_bO_\gamma}{dt}
\]

Equations 4 – 7 may be able to cover all the decomposition modes, such as pyrolysis, dry torrefaction, wet torrefaction, and hydrothermal treatment. Hence, the set of Equations 4 – 7 can be used to calculate the reaction trend lines, i.e., dehydration, decarboxylation, or a combination of these reactions. If these equations are only applied to torrefaction, Equations 5 – 7 can be simplified into Equations 8 – 10.

\[
\frac{dH}{dt} = 2\frac{dH_2O}{dt} \\
\frac{dC}{dt} = \frac{dCO}{dt} + \frac{dCO_2}{dt} \\
\frac{dO}{dt} = \frac{dH_2O}{dt} + 2\frac{dCO}{dt} + \frac{dCO_2}{dt}
\]

By introducing Equations 8 – 10 into Equation 4, Equation 11 is derived.

\[
\frac{d}{dt}\left[\frac{H}{C}\right] = 2\frac{dH_2O}{dCO} \left(\frac{H}{C}\right) \\
\frac{d}{dt}\left[\frac{O}{C}\right] = \left(\frac{dH_2O}{dCO} + 2\right) \left(\frac{O}{C}\right)
\]

The Equation 11 is then simplified to Equation 12.

\[
\text{Slope} = \left(\frac{H}{C}\right) = \frac{2\frac{dH_2O}{dCO} \left(\frac{H}{C}\right)}{\left(\frac{dH_2O}{dCO} + 2\right) \left(\frac{O}{C}\right)}
\]

This equation can be used to estimate the slope of a reaction trend line for torrefaction process based on the amount of H\(_2\)O and CO\(_2\) during torrefaction.

**DISCUSSION**

**Equation validation**

The H\(_2\)O/CO\(_2\) ratio reported ranges from 4 to 90 [16], [24], [25]. Therefore, the slope calculated from Eq. 12 is tabulated in Table 1 with cellulose (r) as the origin/raw material (H/C=10/6=1.67, O/C=5/6=0.83).

To compare the relationship between calculated and experimental results, the reaction of the trend lines were calculated and drawn in Figure 4 based on Eq. 12. Cellulose (r) was taken as the origin for the calculation in Equation 12. The H\(_2\)O and CO\(_2\) ratios are obtained from Prins et al. [16], Zanzi et al. [24], and Mei et al. [25]. Other information data such as initial point (raw material) and final point (decomposed product) were obtained from these literatures as well. The arrows were drawn from the initial (raw material) of each material obtained to the O/C atomic ratio of each product with a slope calculated from Equation 12. From Figure 4, the reaction trend lines are well presented the trend of the product based on the volatile material collected. The discrepancies between the calculated line and the experimental results may come from the assumption that only H\(_2\)O and CO\(_2\) are produced during the torrefaction process. For example, Prins et al. [16] states that in his study, the volatiles contained carbon dioxide, carbon monoxide, water, acetic acid, and other organics. Torrefaction of wood at 300°C produced more acetic acid and other organics than that of 250°C, i.e., 0.071 and 0.266 kg/kg organic for torrefaction at 250 and 300°C, respectively. Hence, the predictive line at 300°C is farther from the experimental point than that at 250°C. Similarly, the mass yield of organics obtained from the torrefied root corn increased with the increase in treatment temperature [25]. In general, this equation is applicable to represent the reaction trend line for torrefaction process. The extension for the general case, which includes pyrolysis, torrefaction, and hydrothermal treatment, is based on the set of Equations 4 – 7.
Table 1  The relationship between H$_2$O/CO$_2$ ratio with the slope of reaction line

<table>
<thead>
<tr>
<th>H$_2$O/CO$_2$ (molar ratio)</th>
<th>The slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-1.16</td>
</tr>
<tr>
<td>0.2</td>
<td>-0.93</td>
</tr>
<tr>
<td>0.3</td>
<td>-0.73</td>
</tr>
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<td>0.8</td>
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<td>0.06</td>
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<tr>
<td>70</td>
<td>1.94</td>
</tr>
<tr>
<td>90</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4  Calculated trend obtained from Equation 12 from this study and experimental results of torrified biomass from literature [16], [24], [25]. The points are experimental data obtained from literature, the arrows are calculated reaction line. The arrow’s slopes are calculated following Equation (12) with cellulose as origin H/C and O/C (H/C=1.67, O/C=0.83) in the calculation.
Development of reaction trend lines in van Krevelen diagram

As previously mentioned, the set of Equations 4 – 7 is generally applied for various decomposition modes, such as pyrolysis, torrefaction, hydrothermal treatment. By assuming the reactions which occur during thermochemical decomposition, one can calculate the trend line of these reaction. Figure 5 shows the development trend lines of some reactions such as dehydration, decarboxylation, decarbonylation, and demethanation. The slope hydration line is always constant and has a value of 2 while the slopes of others reaction lines change depending on raw material (the point 1, 2, and 3). The slope of a specific reaction keeps constant when the initial points fall within that line (point 1 and 2; point 3 and 1). In conclusion, the set of equations can also present the combination of reactions based on the details analysis of volatiles compounds as well.

CONCLUSIONS

In this paper, the authors attempted to formulate a theoretical equation representing a slope in van Krevelen diagram for thermochemical decompositions of biomass. A theoretical equation for this slope was derived based on the removal rates of volatile products during thermochemical decomposition. The relevance of this equation has been proved by using the torrefaction data reported previously. The equation developed in this study will give more insights for the relationship between the trajectory in van Krevelen diagram and the amount of volatile products.
REFERENCES


AUTHORS' INFORMATION

Thanh Hoai Trinh is a Postdoctoral researcher at Universiti Teknologi PETRONAS (UTP). He had worked for Ho Chi Minh City University of Technology, Vietnam for 14 years. Besides that, he cooperated with Agilent and Bruker in Vietnam as a customer support, being responsible for chromatography applications, FT-IR and FT-NIR applications. He obtained his PhD in Chemical Engineering in 2016 from Universiti Teknologi PETRONAS (UTP). He was a Postdoctoral Researcher Fellow at CBBR, UTP for 2 years, and is involved in the research on biomass conversion into fuels and electricity.

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