Pyrolysis and Carbon Dioxide Gasification Kinetics of Pine Cones and Lignite Blends

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Abstract. This study determines the kinetic parameters of blended *Pinus kesiya*, *Pinus elliottii*, and Indonesian lignite in co-pyrolysis and co-gasification. Nine binary blends and three ternary blends were tested using a thermogravimetric analyzer. Pyrolysis was carried out in an argon atmosphere and DTG plots showed that *Pinus kesiya* had the highest maximum pyrolysis rate while *Pinus elliottii* had the lowest starting decomposition temperature. Similarly, blends with *Pinus elliottii* had lower maximum pyrolysis rates and lower starting decomposition temperatures than those with *Pinus kesiya*. Ternary blends, however, have starting decomposition temperatures and maximum pyrolysis rates close to those of pure *Pinus elliottii*. The Kissinger-Akahira-Sunose (KAS) model was used to obtain the reaction rate constants and activation energies of the pyrolysis reactions of various blends. Co-gasification of the mixtures was also done in a CO$_2$ environment at gasification temperatures of 700°C, 800°C, and 900°C. The conversion-time data obtained were fitted using five different gas-solid reaction models.

Introduction
The Philippines relies heavily on imported fossil fuels for power generation, with coal comprising 44.5% as of 2015, up from 37% in 2011. In 2016, coal imports totaled 20.03 million metric tons (mmt), outpacing local production of 12.087 mmt according to the report of the Department of Energy in 2017. As fossil fuel depletion continues, more research into renewable energy sources is being done. One of the more promising sources is biomass, which is the third largest energy source after coal (Chen et al., 2012). Using biomass alone as a replacement for coal is currently not feasible. Although biomass is sustainable, it has a low net efficiency ranging from 20-40% when fired directly (Caputo et al., 2005). The seasonal supply of biomass is another limitation. Co-conversion answers these problems by utilising biomass and coal together as a fuel source, allowing both to compensate for each other’s disadvantages. The low energy density and high tar content of biomass is offset by coal, which has higher calorific value and enhances tar cracking. Because biomass has lower sulfur, nitrogen, and heavy-metal levels, lesser pollutants are emitted when a fraction of coal is replaced with biomass (Tchappda & Pisupati, 2014).

An under-utilized biomass source in the Philippines are cones from pine trees, such as the well-known Benguet pine, also known as *Pinus kesiya*, which thrives in the Luzon tropical pine forest and is widely distributed from Southeast Asia to Africa (Farjon, 2010) where it is also cultivated in plantations. An annual cone-bearer, this species is a relatively fast grower, producing seeds by 5-6 years of age (Nyunaï, 2008). It has a status of Least Concern at the International Union for Conservation of Nature and Natural Resources (IUCN) database of threatened species, making it available for commercial use.

Although co-pyrolysis and co-gasification of fuel-biomass blends is a rapidly-developing research area, there have been no studies on a lignite-pine cone combination. As such, it is necessary to study the behavior of these biomass materials when pyrolyzed and gasified with lignite coals. Previous studies (Font et al., 2008) have shown that cones of *Pinus pinaster* and *Pinus nigra* contains more 90% of total cellulose, lignin, and hemicellulose which, according to Wu et al (2014), potentially creates synergistic effects when reacted thermally with coal. In addition, the minerals in biomass have been found to catalyze these synergistic effects between biomass and coal (Collot et al., 1999).
In this paper, pine cones will undergo co-conversion with lignite. Lignite, also known as brown coal, comprises almost 40% of world coal reserves (Huang et al., 2011), and is distinguished from other coal grades due to its substantially lower calorific content. Its lower price makes it attractive to third-world countries like the Philippines which imports it mainly from Indonesia, while the Philippines itself has 316 million tons of economically recoverable coal, with 105 million tons being lignite. The high sulfur and moisture content of lignite makes its direct combustion problematic. Moreover, the higher reactivity of lignite in comparison with higher-rank coals makes it suitable for gasification (Beamish et al., 1998; Ye et al., 1998).

Methods
This study utilized Pinus kesiya and Pinus elliottii pine cones and Indonesian lignite. The pine cones were obtained locally from pine tree plantations, while the lignite was purchased from commercial sources. Cone and lignite samples were crushed to obtain particle sizes of no greater than 250 μm. The pine cone and lignite particles were mixed according to the desired composition which typically ranges from 10% to 50% lignite with the remaining fraction as pine cones for binary mixtures. For ternary mixtures, same fractions of lignite were used with the two species of pine cones present in equal proportions. The mixture of these components were treated with water to form a slurry and heated for 24 hours in a convective oven at 70°C.

Pyrolysis and gasification reactions were performed in a thermogravimetric analyzer (TGA Q50, TA Instruments) using approximately 10 mg of samples. In the TGA, moisture was initially removed for one hour at 110°C under argon (Ar) environment. The temperature was then ramped at a rate ranging from 20°C/min - 80°C/min to observe pyrolysis and upon attaining a constant weight, Ar-CO2 gas mixture was introduced to initialize gasification. Gasification was observed from 700°C - 900°C. The unreacted char after gasification was determined using Ar-air mixture for its complete combustion.

Thermogravimetric data were used to obtain the starting decomposition temperature and compare the remaining sample fraction against temperature. Then differential thermogram (DTG) data was used to evaluate the maximum decomposition temperature and maximum pyrolysis rate of each sample. To determine the kinetic parameters, specific degrees of conversion were set and the corresponding heating rate and temperature at the set degrees of conversion were obtained. This would yield the value of the independent variable 1/T and the dependent variable, ln β/1/T, with k defined by the model used. The linearized plots of the isoconversion models were tested for goodness of fit by evaluating the coefficient of determination (R²) for a particular model and degree of conversion. The gasification section of the TGA data was isolated and fitted using various gas-solid reaction models. Starink-1.95, Ozawa-Flynn-Wall (OFW), and Kissinger–Akahira–Sunose (KAS) models were used to simulate the pyrolysis reactions. For the gasification of the samples, the homogeneous (HM), shrinking-core (SCM), random pore (RPM), modified volumetric (MVM) and extended modified volumetric (EMVM) models were used to simulate the gasification reactions.
Table 1 shows the proximate analysis of the samples and their corresponding blends.

| Blends                        | Moisture | Volatile Matter | Fixed Carbon | Ash |
|-------------------------------|----------|-----------------|--------------|-----|
| Pure Samples                  |          |                 |              |     |
| *Pinus elliottii*             | 6.57     | 78.37           | 12.16        | 2.91|
| *Pinus kesiya*                | 3.42     | 79.13           | 15.78        | 1.67|
| Indonesian Lignite            | 13.59    | 36.00           | 45.30        | 5.11|
| Binary Blends (elliottii series) |        |                 |              |     |
| 50% *elliottii* + 50% lignite | 5.33     | 58.65           | 31.67        | 4.35|
| 70% *elliottii* + 30% lignite | 4.72     | 64.48           | 27.74        | 3.06|
| 90% *elliottii* + 10% lignite | 2.55     | 66.95           | 28.48        | 2.02|
| Binary Blends (kesiya series) |          |                 |              |     |
| 50% *kesiya* + 50% lignite    | 2.11     | 60.33           | 34.40        | 3.16|
| 70% *kesiya* + 30% lignite    | 5.25     | 61.21           | 30.11        | 3.43|
| 90% *kesiya* + 10% lignite    | 6.62     | 64.31           | 27.27        | 1.8 |
| Ternary Blends                |          |                 |              |     |
| 25% *kesiya* + 25% *elliottii* + 50% lignite | 4.04 | 55.38 | 38.00 | 2.58|
| 35% *kesiya* + 35% *elliottii* + 30% lignite | 3.88 | 59.83 | 34.14 | 2.15|
| 45% *kesiya* + 45% *elliottii* + 10% lignite | 7.72 | 63.53 | 26.36 | 2.39|

Results and Discussion

Samples containing varying amounts of pine cones and lignite were pyrolyzed and gasified and observations were made regarding the thermogravimetric profiles, degradation behavior, and kinetic parameters of the samples.

Pyrolysis characteristics of binary samples

The initial decomposition temperature (IDT) of the binary samples was found to increase with higher heating rates. This is because at high heating rates, heat transfer becomes more inefficient, thus higher temperatures are required for the sample to reach the maximum mass loss rate. The similarities in the IDT of the binary blends with those of the pure pine cones show that biomass governs the degradation characteristics of the blends, even at different biomass loadings. Similar to the pure samples, blends containing *Pinus elliottii* reach maximum degradation point at much lower temperatures than *Pinus kesiya*, the difference ranging from 10°C to as high as 40°C. The effect of heating rate to the binary samples is increased temperature at the same remaining fraction of binary samples. This trend is observed for all binary samples and is due to the limitations of heat transfer. As explained by Wang et al. (2013), at higher heating rates, heat transfer efficiency decreases, requiring higher temperature to consume the same amount of material. Figure 1 shows the typical effect of increasing the heating rates to some selected blends.

![Figure 1](image1.png)

(a) 90% *kesiya* + 10% lignite  
(b) 70% *kesiya* + 30% lignite

The shapes of the DTG curves are almost identical to the pure pine cone DTG curves, with the peaks and shoulders in the same places. The profiles are still nearly identical except height of the maximum peak has decreased as shown by the change in the axis, and the lignin curve immediately
after the cellulose peak has risen from around 5mg/min. to 10mg/min. These changes become more evident with increased lignite content at 50% lignite, where the lignite plateau has risen to almost half the peak point due to addition of the lignite, and passive pyrolysis extends farther than 900°C especially at 80°C/min. The profile is also wider and more symmetrical while retaining the hemicellulose decomposition shoulder. This combination of features is consistent with the study of Zhu et al. (2014) which concluded absence of synergy in the co-pyrolysis of biomass and coal. Figure 2 shows the typical DTG curves of selected binary mixtures.

The activation energies and frequency constants for binary samples of Pinus kesiya, Pinus elliottii, and lignite were evaluated using the Starink-1.95, Ozawa-Flynn-Wall (OFW), and Kissinger–Akahira–Sunose (KAS) models, respectively. These parameters are calculated at varying degrees of conversion for three temperatures: 700°C, 800°C, and 900°C respectively. It can be observed that the activation energy generally decreases with increasing degrees of conversion. At higher degrees of conversion the temperature is also higher, thereby allowing bonds to be broken more easily resulting in this effect. Also, in almost all of the models, blends of Pinus elliottii have lower mean activation energies than blends of Pinus kesiya which makes it more attractive as a biofuel source. There is also a general trend of decreasing frequency factor with increasing degrees of conversion, similar to activation energy. This relationship is also exhibited in the data for pyrolysis of Camel grass in the study of Mehmood et al., (2017) using OFW and KAS models. This is because activation energy is directly related to the frequency factor; this phenomenon is called the kinetic compensation effect, and also explains the linearity between \( \ln A \) and the activation energy. The term compensation is used because an increase in activation energy, which poses a barrier, is surmounted or compensated for by the accompanying increase in frequency factor (Liu et al., 2011). Of the three models, KAS on average has the largest spread from the mean activation energy with average standard deviation of 11.56, 19.91, and 21.81 kJ/mol in contrast with OFW which has 10.95, 18.81, and 20.39 kJ/mol standard deviation for 900°C, 800°C, and 700°C.

Pyrolysis characteristics of ternary samples
For the highest heating rate conducted in this study, the initial degradation temperature (IDT) ranges from a minimum of 250°C for the 35-35-30 blend to 270°C for the 45-45-10 blend, while for the lowest heating rate, the same trend is observed with the 35-35-30 blend having the lowest IDT at 220°C and 45-45-10 blend having the highest IDT at 240°C. The general trend is that higher heating rates results in higher initial degradation temperatures, which means delay in the onset of pyrolysis. As shown in Figure 3, it can be observed that the TG curve drops steeply until around 400°C, at which it slopes off to the maximum pyrolysis temperature. The location of these inflection points in the curve is similar to those of binary blends with respect to the fraction remaining. The inflection point for 45% kesiya + 45% elliottii + 10% lignite is at approximately 0.28, compared to 0.35 for 35% kesiya + 35% elliottii + 30% lignite. For 25% kesiya + 25% elliottii + 50% the curve is very similar to that of lignite. These characteristics resemble binary blends and indicate additive behavior.
All three blends have the highest decomposition temperature at the highest heating rate. The blend 45% *kesiya* + 45% *elliottii* + 10% lignite has the lowest maximum decomposition temperature at all three heating rates, which is a positive indication of viability for pyrolytic fuel. This also shows that *Pinus elliottii* effects are manifested even though it is blended equally with *Pinus kesiya*. Figure 4 shows the typical DTG curves of selected binary mixtures.

For each pyrolysis temperature and heating rate, the 45% *kesiya* + 45% *elliottii* + 10% lignite blend has the lowest activation energy. Generally, however, at higher values of conversion, the activation energy and frequency factor decrease correspondingly. Also, the pyrolysis temperature and the average activation energy exhibit a direct relationship. As the final pyrolysis temperature increases, the activation energy decreases for all ternary blends.

**Gasification of pine cone and lignite blends**

This blend which contains 90% *kesiya* + 10% lignite shows no difference from previous blends. Only 900°C was able to maintain complete conversion; while, both 700°C and 800°C only resulted to approximately 76% and 24% conversion respectively. No significant difference in the conversion was observed as the pine cone content was increased from 70% to 90%.

Generally, all gasification models follow the same trend of increase in parameter, the greater the magnitude of the temperature subjected. In addition, all models show very high $R^2$ coefficients indicating that it can apply to any of the models being used.
In terms of the gas-solid reaction models used, gasification of both *elliottii* and *kesiya* can be simulated using the RPM and SCM models. RPM is heavily favored for the *elliottii* series while SCM for the *kesiya* series in general. This is because porous diffusion is more prominent in the *elliottii* series due to the ash produced, while varying surface area is more protruding for the *kesiya* series. Although there is a slight change in best model for each blend as shown by the HM and RPM for the *elliottii* and *kesiya* respectively, both the RPM for *elliottii* and SCM for *kesiya* still produces of good fit. The activation energy obtained ranges from 144.813 kJ/mol to 198.813 kJ/mol. From this, it can be observed that the activation energy generally increases with increase in percent biomass in the blend. This trend is similar to the binary blends. However, the activation energies obtained from the ternary blends reached values higher than the activation energy of pure Indonesian lignite (173.95 kJ/mol). Only the activation energies obtained from RPM exhibited values lower than that of pure Indonesian lignite. Thus, the ternary blends are not viable for augmenting the Indonesian lignite.

**Conclusions**

In evaluating the effect of feedstock on co-pyrolysis, pure *Pinus kesiya* and blends containing *Pinus elliottii* had the highest maximum pyrolysis rate. Among the binary samples, blends containing *Pinus elliottii* had lower initial decomposition temperatures, lower activation energies and lower maximum pyrolysis temperatures compared to those containing *Pinus kesiya*. The Kissinger-Akahira-Sunose (KAS) model was proven to best simulate the experimental data. For ternary blends, 45% *kesiya* + 45% *elliottii* + 10% lignite had the lowest activation energy in most runs. Having no observable trends on the activation energies of binary and ternary blends at different blend ratios, any synergistic effect was not conclusive. For gasification, maximum carbon conversion increases with increase in temperature. It was also found that EMVM and MVM have almost equal parameters which could be due to their empirical nature. The RPM is the closest to attaining realistic assumptions of gasification as possible with the coal char being assumed to be controlled by pore diffusion kinetics.

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