Pyrolysis Kinetics of Rice Husk in Different Oxygen Concentrations

Wan-Fu Chiang1; Hung-Yuan Fang2; Chao-Hsiung Wu3; Ching-Yuan Chang4; Yu-Min Chang5; and Je-Lueng Shie6

Abstract: The effects of oxygen on the pyrolysis of rice husk were investigated with a thermal gravimetric analysis (TGA) reaction system. Pyrolysis experiments of rice husk were carried out in N2, 10% O2, and air at the heating rates of 2, 5, and 10 K/min. The TGA curves indicated two principal reactions, distinguished by significant and distinct mass changes over the experimental range. Oxygen enhanced the pyrolysis reactions of intermediates, which was produced from the first stage reaction of rice husk. A simple kinetic model was proposed for the pyrolysis of rice husk in different oxygen concentrations. The corresponding activation energies, preexponential factors, and reaction orders were determined. The experimental results were satisfactorily fitted by the proposed kinetic model.


CE Database subject headings: Oxygen; Kinetics; Models; Recycling; Crops; Taiwan.

Introduction

Rice is one of the major crops in Taiwan. There is about 300,000 t of rice husk produced after milling every year. The disposal of vast amounts of rice husk has been one of the major problems facing the rice milling industry. Rice husk is a cellulosic materials, consisting of about 20–35% cellulose, 15–30% hemicellulose, 5–10% lignin, and some minerals. Because rice husk is a renewable source of energy, with a high calorific value of about 4,260 kcal/kg on a dry basis, it may be treated by the pyrolysis methods to obtain fuels (Islam and Ani 2000; Williams and Nugrana 2000) or chemicals as well as to reduce the emission of greenhouse effect gas CO2 and the air pollutants caused by open burning. Besides, rice husk turned out to be a perspective and cheap raw material for production of SiC, SiO2, Si2N2O, Si3N4 or chemicals as well as to reduce the emission of greenhouse effect gas CO2 and the air pollutants caused by open burning. Besides, rice husk turned out to be a perspective and cheap raw material for production of SiC, SiO2, Si2N2O, Si3N4

Patnaik 1995), soil amender (Shinogi and Kanri 2003), and carbon anode materials of lithium-ion batteries (Fey and Chen 2001).

For studies on the pyrolysis products of rice husk, Raveendran et al. (1995) investigated the influence of mineral matter on the product characteristics. From the experimental results, it was concluded that ash present in rice husk seemed to have a strong influence on both the pyrolysis characteristics and the product distribution. The liquid yield increased and gas yield decreased for the de-ash samples. A correlation was developed to predict the influence of ash on volatile yield in their study. Williams and Nugrana (2000) explored the effects of catalysts on the pyrolysis products. In their experiments, rice husks were pyrolyzed in a fluidized bed reactor at 673, 723, 773, 823, and 873 K with/without zeolite ZSM-5 catalyst. The results showed that oxygenated compounds in the oils consisted mainly of phenols, cresols, benzenediols, guaiacol, and their alkylated derivatives. The influence of the catalyst was to convert the oxygen in the pyrolysis oil to largely H2O at the lower temperatures and to largely CO and CO2 at the higher temperatures. Mansaray and Ghaly (1998) investigated the thermal degradation rates of four kinds of rice husks in nitrogen atmosphere between ambient temperature and 973 K. The results indicated that the higher the cellulosic content of rice husk, the higher the thermal degradation rate and the initial degradation temperature. Rice husk could be degraded to the extent of 56–64%. Rao and Sharma (1998) investigated the pyrolysis behavior of rice husk. The experimental results showed that the pyrolysis rates of rice husk could be predicted from the species compounds (cellulose, hemicellulose, and lignin). Sharma and Rao (1999) determined the kinetic parameters for the pyrolysis of rice husk in both grain and powder. Experiments were carried out for rice husk grain and powder samples in N2 and for rice husk grain samples in CO2 at heating rates of 5, 10, 25, 50, and 100 K/min. It was found that the pyrolysis reaction proceeded in two temperature zones with transition at a temperature of 623 K. Reaction orders obtained were 1.5 below 623 K and 2 above this temperature. Vlaev et al. (2003) investigated the pyrolysis mechanisms of rice husk in air or N2. The reaction kinetic parameters were determined. The diffusion control of the pyrolysis process was explained with the high strength of the Si–O carress of the
rice husk which impeded the release of volatile products.

The results of previous studies provided some knowledge about the degradation mechanisms, the effects of ash/catalysts on pyrolysis products, and the kinetic parameters for pyrolysis of rice husk in N2 or CO2. In the commercial process, the partial oxidation of rice husk may be controlled adequately to supply the energy needed in the pyrolysis system. The effects of oxygen concentration on the pyrolysis kinetics need to be discussed in detail. Thus the aim of the present study was to investigate the effects of oxygen on the pyrolysis reaction of rice husk for providing a simple kinetic model for engineering purposes. The pyrolysis of rice husk was studied with a thermal gravimetric analysis (TGA) reaction system. The experiments were carried out in N2, 10% O2, and air at heating rates of 2, 5, and 10 K/min. A two-stage kinetic model was proposed for the pyrolysis of rice husk. The corresponding activation energies, preexponential factors, and reaction orders were determined for the range of experimental conditions. All these results are useful for the pyrolytic treatment of rice husk as a resource.

**Experiment**

**Pyrolysis Apparatus and Procedures**

The Japonica rice husk was used in this study and sampled from the milling plant of Tai-Chung county of Taiwan. Experiments for the pyrolysis of rice husk were carried out with a TGA reaction system as shown previously (Wu and Chang 2001). An electrical balance with 0.01 mg readability was used. A sample of known mass was placed on a small quartz disk 2 cm in diameter and 1 mm thick, hung on suspension wire (platinum, 0.18 mm diameter) of the balance, and enclosed in a quartz reactor. The reactor was 67 cm long with 3.7 cm inside diameter. The carrier gas of 10% O2 was prepared by mixing N2 and air using the mass flow rate controllers. The carrier gas (N2, 10% O2, or air) at a high flow rate was first introduced into the rear channel of the balance cover for 2 h to purge residual gases. It was then adjusted to the desired flow rate of 70 cm3/min. After about 0.5 h, the reactor was placed in a 1.28 kW furnace, which had been preset to a specified heating rate (2, 5, or 10 K/min). The samples were dried to constant mass at 378 K before starting pyrolysis at a specified heating rate. The reaction temperature and mass of sample were recorded at time intervals of 10 s by the computerized data-processing unit. The pyrolysis process was operated under atmospheric pressure. The effluent stream leaving the reactor was passed through a water trap before venting to a fume hood. When pyrolysis had ended, the furnace was turned off and the reactor was dismantled. The sampling temperature Tp=873 K for the pyrolysis of rice husk in N2, 10% oxygen, and air, respectively. However, Tp=873 K was not an end temperature of the second mass change stage for pyrolysis in N2. The sampling temperature (T=873 K) taken the same as that in 10% oxygen and air could provide a common basis for comparing the results.

Elemental compositions (C, H, N, O, S, and Cl) of the combustibles of sample or the pyrolysis residues were determined with an instrumental analyzer. C, H, N, O, and S were determined by the CHN-OS Rapid (Germany) elemental analyzer. Cl was determined by the combustion-titration method (NIEA, 21C, EPAROC). Triplicate experimental runs were carried out for the analysis of C, H, N, O, S, Cl of the initial sample and pyrolysis residues. Inductively coupled plasma atomic emission spectrometer (ICP-AES) (Germany Kontron S-35) was used to quantify some major metals in the sample or pyrolysis residues. The sample or pyrolysis residues mixed with strong acids (2 cm3 HNO3, 0.5 cm3 HClO4, and 1 cm3 HF) were digested at 443 K for 6 h. It was then diluted to 100 cm3 with pure H2O and analyzed by the ICP-AES.

**Results and Discussion**

**Effects of Oxygen on Pyrolysis of Rice Husk**

The properties of rice husk sample are listed in Table 1. The rice husk consists mainly of cellulose, hemicellulose, lignin, and inorganic material. The percentages of the major elements C, H, and O in combustibles were about 39.71, 5.76, and 37.55%, while Si and K in ash were 15.29 and 0.68%, respectively. The high heating value on a dry basis was 4,260 kcal/kg.

The pyrolysis of rice husk in different oxygen concentrations...
Elemental analysis of ashd

Elemental analysis of combustiblec

Combustion was insignificant for the pyrolysis of rice husk in N2.

Two-stage reaction. However, the peak rate of second stage reaction changed with temperatures for various conditions. The reaction temperatures corresponding to the maximum rates were 600, 580, and 585 K for the first stage pyrolysis of rice husk in N2, 10% O2, and air, respectively. It also indicated that the pyrolysis of rice husk was a two-stage reaction. However, the peak rate of second stage reaction was insignificant for the pyrolysis of rice husk in N2.

The final residual masses (Wf) were about 31.69, 34.90, and 34.54% for the pyrolysis of rice husk in N2, 10% O2, and air, respectively. Solid residues, at some specific extents of mass change, were collected and analyzed for determining the effects of oxygen on the pyrolysis of rice husk. The results of elemental analyses are summarized in Table 2, indicating that C, H, and O were still the major constituents of pyrolysis residues. The C/H ratios of final residual masses (at T=873 K) were about 32.03, 27.66, and 38.75% for the pyrolysis reactions in N2, 10% O2, and air, respectively.

For pyrolysis in N2, the total combustibles (C, H, N, O, and S) in residues reduced only 6.08% from the end of the first stage to T=873 K (38.39–32.31%). However, with pyrolysis in 10% O2 and air, they reduced 14.68% (39.22–24.54%) and 13.46% (37.44–23.98%), respectively. The amount decreased for the second stage reaction in oxygen environment and was contributed mainly by the mass changes of C, H, and O, especially for O. It may be ascribed to the reaction of oxygen in the carrier gas with the pyrolysis products of intermediates and resulted in the C–C, C–O, and C–H bond ruptures of intermediates at a higher temperature range (Kilzer and Broido 1965; Reed 1981). This phenomenon can be further supported by the decomposition mechanisms of its main constituents (cellulose, hemicellulose, and lignin) in the following section.

**Kinetic Model**

The common method used for dealing with the pyrolysis data was primarily based on the equation

\[ \frac{dM}{dt} = \frac{(W_0 - W_f)}{W_0} \]

where \( M \) is the mass fraction of rice husk at HR=5 K/min is shown in Fig. 1. The residue with a mass of W after pyrolysis was expressed on a normalized basis as residual mass fraction \( M = \frac{(W - W_f)}{(W_0 - W_f)} \), where \( W_0 \) and \( W_f \) are the initial sample mass and the final residual mass, respectively. Obviously, there were two principal reactions as distinguished by the two significant and distinct mass changes over the reaction temperature range for different oxygen concentrations. When the temperature reached about 450 K, the first distinct mass change began and proceeded very slowly when the residual mass fraction (\( M \)) exceeded 0.9. When \( M \) fell below 0.9, the mass change proceeded rapidly until \( M \) was about 0.5 and then slowly. The second distinct mass change began at a residual mass fraction of about 0.4 and proceeded slowly to the end. Oxygen enhanced the pyrolytic reaction of the rice husk at the higher conversion range (\( T > 600 \) K).

The degradation rates \( r = \frac{dX}{dt} \), with conversion \( X = \frac{(W_0 - W_f)}{(W_0 - W_f)} \), of rice husk at HR=5 K/min is shown in Fig. 2. The maximum rates occurred at different reaction temperatures for various conditions. The reaction temperatures corresponding to the maximum rates were 600, 580, and 585 K for the first stage pyrolysis of rice husk in N2, 10% O2, and air, respectively. It also indicated that the pyrolysis of rice husk was a two-stage reaction. However, the peak rate of second stage reaction was insignificant for the pyrolysis of rice husk in N2.

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\[ \frac{dX}{dt} = \frac{X}{(1 - X)} \]

![Fig. 1. Effects of oxygen on pyrolysis of rice husk at HR=5 K/min](image-url)
\[ r = \frac{dX}{dt} = k(1 - X)^n \]  

where \( r \) = instantaneous reaction rate; \( X \) = conversion at time \( t \); \( n \) = reaction order taking into account the pyrolysis reaction; and \( k \) = reaction rate constant depending on the pyrolysis temperature according to the Arrhenius relation, \( k = A \exp(-E/RT) \).

The differential method for determining the activation energy (\( E \)) was employed in this study. Taking the natural logarithm of both sides of the Eq. (1) yielded \( \ln(\frac{dX}{dt}) = \ln[A(1-X)^n] - E/RT \). At the same degree of conversion, the reaction temperatures were different at different heating rates. A desired residual mass fraction (or conversion) was specified from the TGA curves (Figs. 3–5), and then the reaction temperatures corresponding to the various heating rates were obtained. Simultaneously, a set of instantaneous rates (\( \frac{dX}{dt} \)) was deduced corresponding to these reaction temperatures from the instantaneous reaction rate curves. A straight line with slope \((-E/R)\) was obtained by plotting \( \ln(\frac{dX}{dt}) \) versus \( 1/T \). The value of \( E \) corresponding to the selected conversion would then be obtained by multiplying the slope \((-E/R)\) with a negative universal constant \((-R)\).

The activation energies at different conversions are shown in Figs. 6–8. The activation energies might be divided into two groups for each pyrolysis condition. For the pyrolysis of rice husk in N\(_2\), the activation energies were in the range of about 0.2–33.49 kcal/mol. The arithmetic averages of activation energies over the first \((X=0–0.5)\) and second \((X=0.5–1)\) reaction stages were 25.72 \( (E_1) \) and 7.1 \( (E_2) \) kcal/mol, respectively. For the pyrolysis of rice husk in 10% O\(_2\), the activation energies were in the range of about 5.91–62.17 kcal/mol. The

### Table 2. Elemental Analyses of Residues Relative to Initial Sample at Various Pyrolysis Temperatures (Dry Basis)

<table>
<thead>
<tr>
<th>Pyrolysis temperature (K)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>O (%)</th>
<th>S (%)</th>
<th>Total (%)</th>
<th>C/H (wt/wt)</th>
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<tr>
<td>Initial sample</td>
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<td>83.69</td>
<td>6.89</td>
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<td>(0.11)(^a)</td>
<td>(0.12)</td>
<td>(0.05)</td>
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<td>Pyrolysis residues in N(_2)</td>
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<tr>
<td>600</td>
<td>27.16</td>
<td>2.13</td>
<td>0.05</td>
<td>8.69</td>
<td>0.10</td>
<td>38.13</td>
<td>12.75</td>
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<td></td>
<td>(0.09)</td>
<td>(0.06)</td>
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<td>643</td>
<td>26.06</td>
<td>2.31</td>
<td>0.06</td>
<td>9.82</td>
<td>0.14</td>
<td>38.39</td>
<td>11.28</td>
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<tr>
<td>873</td>
<td>22.10</td>
<td>0.69</td>
<td>0.26</td>
<td>9.25</td>
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<td>32.31</td>
<td>32.03</td>
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<td>Pyrolysis residues in 10% O(_2)</td>
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<td>580</td>
<td>26.96</td>
<td>2.28</td>
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<td>10.40</td>
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<td>39.80</td>
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<td>(0.12)</td>
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<td>20.47</td>
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<td>Pyrolysis residues in air</td>
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<td>585</td>
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<td>606</td>
<td>25.83</td>
<td>1.90</td>
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<td>(0.60)</td>
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\(^a\)Values in parentheses are standard deviations.
arithmetic averages of activation energies over the first \( X=0–0.56 \) and second \( X=0.56–1 \) reaction stages were 21.9 \( E_1 \) and 26.4 \( E_2 \) kcal/mol, respectively. For the pyrolysis of rice husk in air, the activation energies were in the range of about 21.2–56.2 kcal/mol. The arithmetic averages of activation energies over the first \( X=0–0.54 \) and second \( X=0.54–1 \) reaction stages were 34.1 \( E_1 \) and 42 \( E_2 \) kcal/mol, respectively.

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The rice husk consists mostly of cellulose, hemicellulose, and lignin together with a small fraction of inorganic material. Cellulose is composed of \( d \)-glucose units \((C_6H_{10}O_5)\) bonded together by ether-type linkages called glycosidic bonds. Most hemicelluloses contain two to four (and occasionally five to six) simpler sugar residues. The \( d \)-xylose \((C_5H_{10}O)\) is the most abundant of hemicellulose (Reed 1981; Chang et al. 1996). According to the decomposition mechanisms proposed by Kilzer and Broido (1965), the reaction of cellulose involved at least three distinct processes for low-temperature pyrolysis. At about 493 K, the first process was attributed to an intermolecular dehydration to form “anhydrocellulose.” At about 553 K, the second process competed with the first process for cellulose pyrolysis and was responsible for the formation of levoglucosan—the major constituent of tar. Levoglucosan was postulated to arise from the rearrangement of 1,4-anhydro-\( d \)-glucopyranose formed in an unzipping/depolymerization reaction. Finally, the third process was ascribed to the decomposition of the “anhydrocellulose” to produce volatile C-containing compounds and hydrogen, and char. The formation of levoglucosan, which was a principal intermediate compound, took place at somewhat higher temperatures and led to further decomposition reactions at elevated temperatures. The pyrolysis mechanisms of hemicellulose were generally postulated by a two-step decomposition scheme (Reed 1981). First, depolymerization to water-soluble fragments occurred, followed by decomposition to volatiles. Generally, the overall pyrolysis behavior of rice husk could be ascribed to the decomposition of hemicellulose in a lower temperature, cellulose at a higher temperature range, and lignin over the entire temperature range (Williams and Besler 1993). Owing to the variety of components in rice husk, the pyrolysis of rice husk would comprise a complex series of concurrent/consecutive chemical decomposition reactions of combustibles. For en-

![Fig. 3. Comparison of residual mass fraction \((M)\) by model prediction (line), with experimental data (symbol) at different heating rates (HR) for pyrolysis of rice husk in \( N_2 \): \( R_2^2, R_5^2, R_{10}^2: 0.996, 0.998, 0.966 \)](image)

![Fig. 4. Comparison of residual mass fraction \((M)\) by model prediction (line), with experimental data (symbol) at different heating rates (HR) for pyrolysis of rice husk in 10% \( O_2 \): \( R_2^2, R_5^2, R_{10}^2: 0.996, 0.993, 0.995 \)](image)
gineering purposes, the numerous reactions may be simplified and lumped together to form a more briefly representative reaction pattern for the determination of kinetic expressions for the pyrolysis of rice husk. Examining the TGA curves of Figs. 3–5 and the distributions of activation energies of Figs. 6–8, one notes that the pyrolysis of rice husk may be expressed as a two-stage reaction.

For the two-stage reaction model, as shown in Fig. 9, there were two principal reactions as distinguished by the two significant and distinct mass changes over the experimental temperature range. Figs. 3–5 suggest that the first stage pyrolysis reaction contributed mainly in the temperature range below about 600–630 K. The residual mass fraction of the pyrolyzed sample decreased from 100 to about 50–56% for the pyrolysis reactions in three carrier gases. The degradation reactions of cellulose, hemicellulose, and lignin of rice husk were considered as an overall reaction. The products of this reaction were intermediates and volatiles at pyrolysis temperature. The second reaction contributed mainly in the temperature range from about 610–630 to 850 K in 10% O₂ and air and to 900–1500 K in N₂. In this reaction, the intermediates further reacted to form volatiles and solid residues. The decomposition of intermediates was also considered as a representative reaction. V₁ and V₂ are the volatiles released from the pyrolysis of rice husk and the intermediates, respectively. For the pyrolysis reactions in 10% O₂ and air, oxygen in the carrier gas may react with volatiles and then enhance the second stage reaction. The residual mass fraction M may be obtained by the following equations:

\[
M = (W - W_f)/(W_0 - W_f) = 1 - m_{v_1} - m_{v_2}
\]  

(2)

\[
d(m_{v_1}/F_1)/dt = k_1[1 - (m_{v_1}/F_1)^{n_1}] 
\]  

(3)

\[
d(m_{v_2}/F_2)/dt = k_2[1 - (m_{v_2}/F_2)^{n_2}] 
\]  

(4)

where \(k_1 = A_1 \exp(-E_1/RT)\) and \(n_1\); and \(k_2 = A_2 \exp(-E_2/RT)\) and \(n_2\) = Arrhenius rate constants and reaction orders of Reactions (1) and (2), respectively, and \(m_{v_1} = W_{v_1}/(W_0 - W_f)\) and \(m_{v_2} = W_{v_2}/(W_0 - W_f)\) = mass fractions of volatiles \(V_1\) and \(V_2\), respectively. Eqs. (2)–(4) satisfy the following conditions:

![Fig. 5. Comparison of residual mass fraction (M) by model prediction (line), with experimental data (symbol) at different heating rates (HR) for pyrolysis of rice husk in air; \(R_2, R_5, R_{10}: 0.996, 0.997, 0.998\)]

![Fig. 6. Activation energies (E) at different conversions (X) for pyrolysis of rice husk in N₂](http://pubs.asce.org/copyright)
In Eqs. (3) and (4), $F_1$ and $F_2$ are weighting factors taking into account the decrease of the residual mass fraction contributed by the pyrolysis Reactions (1) (<610–630 K) and (2) (610–630 to 850–1,500 K), respectively. They satisfy

$$m_{v_1} = F_1 X_1, \quad m_{v_2} = F_2 X_2$$

where $X_1$ and $X_2$ are conversions of pyrolysis Reactions (1) and (2), respectively. From the TGA curves in Figs. 3–5 and the distributions of activation energies in Figs. 6–8, $F_1$ and $F_2$ are estimated to be about 0.5 and 0.5, 0.56, and 0.44, 0.54, and 0.46 for the pyrolysis of rice husk in N₂, 10% O₂, and air, respectively.

Eqs. (3) and (4) were solved to give the following solutions:

$$m_{v_1}/F_1 \equiv 1 - \left\{ [A_1 RT^2 (n_1 - 1)] (1 - 2RT/E_1) \times \exp(-E_1/RT)/E_1HR + 1 \right\}^{1/(1-n_1)}, \quad (n_1 \neq 1) \quad (7)$$

$$m_{v_2}/F_2 \equiv 1 - \left\{ [A_2 RT^2 (n_2 - 1)] (1 - 2RT/E_2) \times \exp(-E_2/RT)/E_2HR + 1 \right\}^{1/(1-n_2)}, \quad (n_2 \neq 1) \quad (8)$$

where HR=dT/dt=heating rate; $A_1$ and $E_1$, and $A_2$ and $E_2$ = preexponential factors and activation energies of pyrolysis Reactions (1) and (2), respectively; and $T$ = pyrolysis temperature.

In this study, the parameters of $E$, $A$, and $n$ were obtained by using the values at heating rates of 2, 5, and 10 K/min. Since the values of activation energy varied with the extent of reaction as shown in Figs. 6–8, it was necessary to select a set of representative kinetic parameters in applying the above equations for engineering purposes. The arithmetic average of activation energies over the conversion ranges of each reaction stage are shown in Table 3. Also, rearranging Eq. (1) and taking natural logarithms, gives

$$\ln[(dX/dt)/\exp(-E/RT)] = \ln A + n \ln(1 - X) \quad (9)$$

With the substitution of the instantaneous rates $(dX/dt)$ and
the average activation energy of each reaction stage into Eq. (9), a straight line with slope \( n \) and intercept \( \ln A \) was obtained by plotting \( \ln[(dX/dt)/\exp(-E/RT)] \) against \( \ln(1-X) \). Thus the reaction orders and the preexponential factors were obtained as listed in Table 3. The reaction orders were \( n_1=1.2 \) and \( n_2=1.89 \) for the pyrolysis in \( N_2 \), \( n_1=1.11 \) and \( n_2=1.65 \) in 10% \( O_2 \), and \( n_1=1.35 \) and \( n_2=1.89 \) in air, respectively. The preexponential factors were \( A_1=7.09 \times 10^8 \) and \( A_2=121.5 \) L/min for the pyrolysis in \( N_2 \), \( A_1=3.22 \times 10^7 \) and \( A_2=2.75 \times 10^7 \) L/min in 10% \( O_2 \), and \( A_1=2.18 \times 10^{12} \) and \( A_2=9.8 \times 10^{12} \) L/min in air, respectively.

For the pyrolysis of rice husk in \( N_2 \), the activation energy of first stage pyrolysis \( (E_1=25.72 \text{ kcal/mol}) \) was higher than that of the second stage pyrolysis \( (E_2=7.1 \text{ kcal/mol}) \). It was similar to the results examined by Sharma and Rao (1999). Their results indicated that the activation energy and preexponential factor values in the lower temperature range (498–623 K) varied from 17 to 24 kcal/mol and \( 3.7 \times 10^7 \) to \( 1.3 \times 10^9 \) while in the higher temperature range varied from 1 to 6 kcal/mol and \( 8.4 \times 10^4 \) to 68.1 L/min. The activation energy values reported by Sharma and Rao (1999) were slightly low compared with the present values. Also, the higher value of \( E \) observed at lower temperature range showed that the initial release of volatile products occurred under kinetic-diffusion control while the much lower value of \( E \) at a higher temperature range indicated that pyrolysis had taken place under diffusion control (Vlaev et al. 2003). Comparing the pyrolysis of rice husk in oxygen environment in this study, similar values of activation energy found for first stage pyrolysis showed that the release of volatile products during pyrolysis in oxygen environment and in nitrogen medium occurred by similar mechanisms. However, the values of activation energies and preexponential factors for pyrolysis in oxygen environment were much higher than those of pyrolysis in nitrogen for the second stage reaction. This may be ascribed to the reaction of oxygen with the products released from the pyrolysis of intermediates resulting in a kinetic-diffusion control reaction.

The values of residual mass fraction computed by the proposed kinetic model were compared with the experimental data, as shown Figs. 3–5. The coefficients of determination, \( R^2 \), \( R^2 \), and \( R^2 \) (computed for the range 5–95% of final weight loss, \( W_0-W_f \), of these curves of \( HR_5 \), \( HR_5 \), and \( HR_5 \) were about 0.966–0.998. The results computed by the proposed model gave a good agreement with the experimental data. To verify the applicability of the kinetic parameters obtained and the validity of the proposed kinetic model, a higher heating rate (20 K/min) was tested to predict the effect of heating rate on pyrolysis at \( N_2 \), 10% \( O_2 \), and air environment. The results are shown in Fig. 10. The coefficients of determination, \( R^2 \), \( R^2 \), and \( R^2 \) were 0.985, 0.996, and 0.995 for pyrolysis in \( N_2 \), 10% \( O_2 \), and air, respectively. This thus supported the validity and practical applicability of the proposed kinetic model for the pyrolysis at a low heating rate range. However, the concentrations of oxygen used in this study were 10 and 20.94% (air) only. The applicability of the proposed model will be limited for a particular oxygen concentration. It is necessary to do the experimental runs with other oxygen concentrations to establish the pyrolysis model including the oxygen concentration as a variable. Also, further works would be helpful to further support the applicability of this model. Such works may include:

### Table 3. Kinetic Parameters of Pyrolysis Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Preexponential factor (L/min)</th>
<th>Reaction order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis in ( N_2 )</td>
<td>( E_1=25.72 )</td>
<td>1.20</td>
</tr>
<tr>
<td>Pyrolysis in 10% ( O_2 )</td>
<td>( E_2=7.10 )</td>
<td>1.89</td>
</tr>
<tr>
<td>Pyrolysis in air</td>
<td>( E_2=21.90 )</td>
<td>1.11</td>
</tr>
</tbody>
</table>

**Fig. 10.** Comparison of residual mass fraction \( (M) \) by model prediction (line), with experimental data (symbol) at heating rate (HR) of 20 K/min for pyrolysis of rice husk in \( N_2 \), 10% \( O_2 \), and air; \( R^2_{20(N2)}, R^2_{20(10\%O2)}, R^2_{20(air)} \): 0.985, 0.996, 0.995
(1) examining the applicability of this model under very high heating rates (say 50 to 500 K/min); and (2) analyzing the detailed pyrolysis products to explore the effects of oxygen on the pyrolysis mechanisms.

Conclusions

Pyrolysis experiments of rice husk were carried out in \( N_2 \), 10% \( O_2 \), and air to investigate the effects of oxygen on the pyrolysis reactions. It was found that there were two principal reactions as distinguished by the two significant and distinct mass changes over the reaction temperature range for all the experimental conditions. Oxygen reacted with the products released from the pyrolysis of intermediates and enhanced the second stage pyrolysis reaction. A simplified two-stage reaction model was proposed to illustrate the kinetic behavior of rice husk over a wide temperature range of 400–1500 K. The kinetic parameters \( E \), \( A \), and \( n \) were determined based on the heating rates of 2, 5, and 10 K/min. The values of \( E \) and \( A \) for pyrolysis in oxygen environment were much higher than those of pyrolysis in nitrogen for the second stage reaction. The kinetic reaction model was tested with a higher heating rate and gave good agreement with the experimental data for the pyrolysis of rice husk in different reaction conditions. The data and model appear to be useful in the design of a rice husk processing system.

Acknowledgments

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Notation

The following symbols are used in this paper:

\[
A = \text{preexponential factor of Arrhenius term (L/min)}; \
A_1, A_2 = \text{A of pyrolysis reactions 1, 2 (L/min)}; \
E = \text{activation energy (kcal/mol)}; \
E_1, E_2 = \text{E of pyrolysis reactions 1, 2 (kcal/mol)}; \
F_1, F_2 = \text{weighting factors taking account of contribution of pyrolysis Reactions 1, 2 ()}; \
HR = \text{heating rate, } =dT/dt \text{ (K/min)}; \
HR_{20}, HR_{5}, HR_{10}, HR_{20} = \text{heating rates of 2.5, 10, 20 (K/min)}; \
k = \text{reaction rate constant, } =A \exp(-E/R T) \text{ (L/min)}; \
k_1, k_2 = k \text{ of pyrolysis reactions 1, 2 } = A_1 \exp(-E_1/RT), A_2 \exp(-E_2/RT) \text{ (L/min)}; \
M = \text{residual mass fraction at time } t, = (W_W - W)/ (W_W - W_f) (); \
m_{V_1}, m_{V_2} = \text{mass fractions of volatiles } V_1, V_2 \text{ based on } W - W_f = W_{V_1} / (W_W - W_f), W_{V_2} / (W_W - W_f) (); \
n = \text{reaction order (); } \
n_1, n_2 = n \text{ of pyrolysis Reactions 1, 2 (); } \
R = \text{universal gas constant, } 1.987 \times 10^{-3} \text{ (kcal/mol K)}; \
R^1 = \text{coefficient of determination, } = 1 - [\Sigma(y - \bar{y})^2] / [\Sigma(y - \bar{y})^2](); \
R^2, R^3, R^4, R^5, R^6 = \text{R}^2 \text{ of } HR_2, HR_5, HR_{10} (); \
r = \text{instantaneous reaction rate, } = dX/dt \text{ (L/min)}; \
T, T_0 = \text{pyrolysis temperatures at time } t, \text{ and at beginning (t=0) of pyrolysis (K)}; \
T_{p}, T_{end1}, T_{end2} = \text{sampling temperatures corresponding to maximum rate, end of first, second mass change stages (K)}; \
T = \text{pyrolysis time, } = (T - T_0) / HR \text{ (min)}; \
V_1, V_2 = \text{volatiles produced by pyrolysis reactions defined as Fig. 9}; \
W, W_0 = \text{total masses of residual sample at time } t, \text{ and of initial sample (mg)}; \
W_f = \text{total final residual mass (mg)}; \
W_{V_1}, W_{V_2} = \text{accumulated masses of } V_1, V_2 \text{ at time } t \text{ (mg)}; \
X = \text{conversion at time } t, = (W_0 - W) / (W_0 - W_f) = 1 - M (); \
X_1, X_2 = \text{X of pyrolysis Reactions 1, 2 (); } \
y = \text{experimental value of residual mass fraction at specified temperature (); } \
y_a = \text{arithmetic average of experimental values of residual mass fraction at specified temperature (); } \
y_c = \text{computed value of residual mass fraction at specified temperature (); }
\]

References


