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Soen Steven

Institut Teknologi Bandung

Pandit Hernowo

Institut Teknologi Bandung

Elvi Restiawaty

Institut Teknologi Bandung

Anton Irawan

Universitas Sultan Ageng Tirtayasa

Carolus Borromeus Rasrendra

Institut Teknologi Bandung

Yazid Bindar (✉ ybybyb@fti.itb.ac.id)

Institut Teknologi Bandung

Research Article

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Posted Date: April 14th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-359990/v1>

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Version of Record: A version of this preprint was published at Waste and Biomass Valorization on January 13th, 2022. See the published version at <https://doi.org/10.1007/s12649-021-01657-x>.

**Thermodynamics simulation performance of rice husk combustion with a realistic decomposition
approach on the devolatilization stage**

Soen Steven¹, Pandit Hernowo¹, Elvi Restiawaty^{1,2}, Anton Irawan⁵, Carolus Borromeus Rasrendra^{1,3}, and Yazid

Bindar^{1,4*}

¹Department of Chemical Engineering

²Research Group on Design and Development of Chemical Engineering Processes

³Center for Catalysis and Reaction and Engineering

⁴Research Group on Biomass and Food Processing Technology

Faculty of Industrial Technology, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia

⁵Chemical Engineering Department, Faculty of Engineering, Universitas Sultan Ageng Tirtayasa, Jl. Jendral
Soedirman km 3 Cilegon, Banten, 42135, Indonesia

* Corresponding author: ybybyb@fti.itb.ac.id

Abstract

Rice husk has a great potential in its calorific value and silica content in ash which makes its valorization through combustion becomes important and interesting. This study presents the thermodynamics simulation performance of rice husk combustion using a realistic decomposition approach. A non-ideal gas approach and fugacity coefficient were also considered in the calculation. From this study, rice husk is devolatilized to form gases (63.37%), tar (8.69%), char (27.94%), and all of these are then oxidized to form flue gas. The realistic decomposition approach calculated that about 2.6 MJ/kg of specific combustion energy is produced, the maximum combustion temperature is up to 1457°C for perfect insulation condition, and up to 1400°C if there is a heat loss. It is found that combustion equipped with larger excess air could quench the heat produced and reduce the combustion efficiency but could maintain the temperature at 700°C. Furthermore, the thermodynamics simulation expressed that NO emission amount from rice husk combustion is negligible and there is still a probability for CO and H₂ to be produced at above 500°C due to Boudouard reaction and homogeneous water gas shift reaction (WGSR). The study showed that a realistic decomposition approach could predict the rice husk combustion performance with a reasonable and logical result. Supplying excess air of about 180-200% is advantageous to keep the combustion temperature at 700°C in order to prevent silica crystalline formation which harms human

health, as well as suppressing NO emission and reducing CO emission from the simultaneous Boudouard and WGSR.

Keywords: Biomass, Degree of freedom, Flue gas, Adiabatic flame temperature, Air to fuel ratio

Statement of Novelty

So far, many established simulations have proposed a simple approach to the devolatilization stage. This is unrealistic because assumes that biomass will decompose to C, H, O, N elements before entering oxidation. In the realistic decomposition approach, biomass is devolatilized not to form C, H, O, N elements but light gases, liquid as tar, and solid as char. Interestingly, there is still a lack of study on it and therefore, This study discussed the rice husk combustion simulation performance with a realistic decomposition approach on the devolatilization stage. The results perform that this approach gives a reasonable agreement with the other researchers' results in terms of specific combustion energy, maximal combustion temperature, and flue gas composition analysis.

1. Introduction

Recently, biomass utilization as an alternative fossil fuel and chemicals surrogates has become a major concern. Rice husk is one of the abundant biomass in Indonesia which occupies approximately 20%-wt from paddy, consists of nearly 20%-wt rice husk ash, contains silica as much as 87%-wt from its ash, and has a calorific value of 14-17 MJ/kg [1–3]. The high calorific value, as well as rich silica in ash, make rice husk important and interesting to be valorized. There are several stages occurred in the rice husk combustion, that is drying, devolatilization, oxidation, and ash formation [1, 4, 5]. So far, energy production through rice husk combustion mostly relied on direct experiments and then validate the results with thermodynamics simulation. They have focused on specific combustion energy calculation, rice husk combustion temperature monitoring, and flue gas composition prediction and analysis.

A study on combined heat power fuelled by rice husk with a maximal temperature of about 1100°C gave a specific rice husk consumption of 1.2-1.7 kg/kWh [6] or recalculated as specific energy produced in the range of 2.12-3.00 MJ/kg. Apart from that, the case study from Pakistan stated that as much as 4947.28 MWh of energy could be generated from 6432 tonnes of rice husk combustion [7] or equal to specific combustion energy of about 2.77 MJ/kg. The energy balance evaluation on 2.8 g/s rice husk combustion for steam and hot air generation resulted

in 21.09 kJ/s of utilized energy [8] and it is equal to 7.53 MJ/kg of specific energy. Meanwhile, the rice husk combustion modelling study in a grate bed furnace had a maximum combustion temperature of 1406.85°C and flue gas exhaust temperature of 693.85°C with the composition of N₂, CO, CO₂, H₂O, and remaining O₂ [9].

The thermodynamics study from the research papers and well-established textbooks mostly proposed that at the devolatilization stage, biomass will decompose to C, H, O, N elements prior to being oxidized to form flue gas [10–12]. This approach is simple but quite unrealistic so that it should be developed with a more realistic one. Realistic decomposition assumes that rice husk devolatilization products are not C, H, O, N elements but gases, tar, and char [10]. Nevertheless, there is still a lack of study on it and therefore, this study intends to discuss the thermodynamics simulation performance of rice husk combustion with a realistic decomposition approach. The discussion comprises of problem preliminary analysis, devolatilized products result, specific energy produced from rice husk combustion, adiabatic flame temperature, air supply strategy for maintaining rice husk combustion temperature, and the flue gas composition analysis due to the attendance of Boudouard reaction and homogeneous water gas shift reaction (WGSR).

2. Methods

2.1. Devolatilized products prediction calculation

In this study, rice husk has a calorific value of 14.95 MJ/kg. The ultimate and proximate analysis results are given in Table 1. The proximate analysis procedure is performed at 900°C follows ASTM 3175-07 procedure, whereas the combustion occurred at $T = 700^\circ\text{C}$.

Table 1. Ultimate and proximate analyses of rice husk

Ultimate Analysis (Dry Basis)		Proximate Analysis (As-received)	
C	37.95%	Moisture	8.98%
H	5.41%	Volatile Matter	58.13%
O	36.56%	Fixed Carbon	15.49%
N	0.96%	Ash	17.40%

A volatile enhancement factor V_E , which is commonly found in 0.8-1.3, plays a role to correct the devolatilized product at a temperature beyond 900°C [10, 11]. To determine V_E , the biomass type number (N_{CT}) should be calculated first as in equation 1a. The N_{CT} value is then applied to determine the predicted volatile matter value (Y'_{VM}), equation 1b. Subsequently, equation 1c is a temperature correction function, $f_5(T)$ in °C unit, which is later employed in equation 1d to obtain the predicted devolatilized products mass fraction (Y'_{VY}). Afterward, V_E is calculated following equation 1e [10, 11]. Rice husk devolatilization produces gases, tar, and char. Gases were

represented with CO, H₂, CO₂, CH₄, HCN, and H₂O. Tar was assumed to consist of C₁₆H₁₈, C₁₀H₁₄O₂, C₇H₈O, and C₉H₇N. Char was presumed to contain only C. Each product amount is determined from equation 2 and should consistent with the value from dry-ash-free basis of proximate and ultimate analysis [10, 11].

$$N_{CT} = \frac{Y_{C,ult}^2}{Y_{H,ult} \cdot Y_{O,ult}} \quad (1a)$$

$$Y'_{VM} = \exp[0.031 - 0.029 \ln N_{CT} - 0.038(\ln N_{CT})^2] \quad (1b)$$

$$f_5(T) = 3.87 \left(\frac{T}{900}\right)^5 - 28.28 \left(\frac{T}{900}\right)^4 + 80.87 \left(\frac{T}{900}\right)^3 - 112.8 \left(\frac{T}{900}\right)^2 + 77.07 \left(\frac{T}{900}\right) - 20.26 \quad (1c)$$

$$Y'_{VY} = Y'_{VM} \cdot \exp[f_5(T)] \quad (1d)$$

$$V_E = \frac{Y'_{VY}}{Y'_{VM}} = \frac{Y_{VY}}{Y_{VM}} \quad (1e)$$

$$Y_{char} = 1 - Y_{VY} = 1 - \sum Y_i \quad (2a)$$

$$Y_{C,ult} = Y_{char} + \sum \left(\frac{Y_{C,i} \cdot Ar_C}{Mr_i} \right) \quad (2b)$$

$$Y_{H,ult} = \sum \left(\frac{Y_{H,i} \cdot Ar_H}{Mr_i} \right) \quad (2c)$$

$$Y_{O,ult} = \sum \left(\frac{Y_{O,i} \cdot Ar_O}{Mr_i} \right) \quad (2d)$$

$$Y_{N,ult} = \sum \left(\frac{Y_{N,i} \cdot Ar_N}{Mr_i} \right) \quad (2e)$$

where Y_{VY} is the actual devolatilized products mass fraction, Y_{VM} is the volatile matter value from proximate analysis on dry-ash-free basis, Y_i is the i^{th} component of actual devolatilized products mass fraction, Y_{char} is the char fraction, $Y_{C,i}$ is the number of C atoms in i^{th} component, $Y_{H,i}$ is the number of H atoms in i^{th} component, $Y_{O,i}$ is the number of O atoms in i^{th} component, $Y_{N,i}$ is the number of N atoms in i^{th} component, Y_{ult} is the C-H-O-N content ultimate analysis in dry-ash-free basis, Ar is the atomic weight for C-H-O-N, and Mr_i is the molecular weight of i^{th} component.

In the rice husk combustor, all devolatilized products react with oxygen from the air. The air amount was varied under stoichiometric and excess conditions. The flue gas temperature was also varied from 200-700°C. The excess air (EA) is calculated from equation 3 and the O₂ and CO₂ percentages in the flue gas are acquired from equation 4, respectively.

$$EA = \frac{n_a - n_s}{n_s} \times 100\% \quad (3)$$

$$O_2 \text{ in flue gas} = \frac{n_{O_2,a} - n_{O_2,s}}{n_{fg}} \times 100\% \quad (4a)$$

$$CO_2 \text{ in flue gas} = \frac{n_{CO_2}}{n_{fg}} \times 100\% \quad (4b)$$

where n_a is the actual air amount; n_s is the stoichiometric air amount; $n_{O_2,a}$ is the actual oxygen amount; $n_{O_2,s}$ is the stoichiometric oxygen amount; and n_{CO_2} is the carbon dioxide amount; and n_{fg} is the flue gas amount.

2.2. Combustion efficiency calculation

Combustion efficiency requires inlet and outlet enthalpy calculation with the reference temperature of 25°C. Inlet enthalpy (H_{in}) was derived from biomass and air inlet enthalpy. Air inlet enthalpy considered residual enthalpy (H^R) from Pitzer-Lee-Kesler Generalized Correlation which involves acentric factor (ω) and critical temperature (T_c) properties [13]. The outlet enthalpy (H_{out}) considered ash and flue gas sensible heat as well as 5% heat loss (H_{loss}) from inlet enthalpy due to radiation. The heat capacity (C_p) for all components was a temperature-dependent polynomial function. All properties constant are adapted from common databanks [13–15]. Combustion efficiency (η_c) is derived from the difference between inlet and outlet enthalpy including heat loss, equation 5 [3].

$$\eta_c = \left(1 - \frac{H_{out} + H_{loss}}{H_{in}}\right) \times 100\% \quad (5)$$

2.3. Thermodynamics calculation procedure

Thermodynamics calculation entangled fugacity coefficient (ϕ) and was determined using a generic cubic equation of state, as served in equation 6. It also involved the compressibility factor (Z) which requires critical pressure (P_c) and was determined using Redlich-Kwong, Soave-Redlich-Kwong, and Peng-Robinson models. The coefficient of β , q , I , Ω , Ψ , α , σ , and ε for the calculation are taken from state parameters assignment [13, 16].

$$\phi = \exp(Z - 1 - \ln(Z - \beta) - qI) \quad (6)$$

The interaction between flue gas with remaining biomass through Boudouard reaction and homogeneous water gas shift reaction (WGSR) were assumed ideal and the calculation was carried out using the Gibbs Energy minimization as seen in equation 7 which considers the temperature-dependent of equilibrium constant (K) and the stoichiometric coefficient of each component (ν_i) [13]. The iterative calculation should be addressed until the error tolerance is below 10^{-6} .

$$\prod_{i=1}^n (y_i \phi_i)^{\nu_i} = K \quad (7)$$

3. Result and discussion

3.1. Problem preliminary analysis: Degree of freedom

In this study, rice husk combustion occurred at 1 bar and feed inlet at 25°C. The combustion is assumed to be complete until remains rice husk ash. The flue gas produced from the combustion, hence, is composed of CO₂, H₂O, NO, N₂, and the remaining O₂ [9]. NO compound, as one of the NO_x constituents, is chosen due to the process condition tends to form NO than NO₂ or N₂O [17]. A preliminary analysis in the form of degree of freedom analysis (DoF) is conducted to determine the problem completion criteria. Figure 1 served the rice husk combustion block diagram embedded with DoF analysis result. It can be seen that DoF value is equal to 0 for both mass balance and mass-energy balance, which implies the problems are well-specified and able to be solved either separately (decoupled) or simultaneously (coupled) [12].

Figure 1. Rice husk combustion block diagram with DoF analysis

3.2. Rice husk combustion calculation result using realistic decomposition

The calculation for air inlet condition should utilize the real (non-ideal) gas approach and for the flue gas exit condition fulfills the ideal gas approach. Flue gas pressure and temperature conditions neglect the intermolecular interactions due to the high kinetic energy, which reflects the ideal gas characteristics [18]. When the temperature becomes lower resembles the inlet condition, kinetic energy becomes low and allows for significant intermolecular interactions [14, 16, 18]. Consequently, a real gas approach for inlet state should be considered. According to the realistic decomposition approach calculation, the V_E value of 0.91 will lead to the actual devolatilized products as schemed in Figure 2.

Figure 2. Rice husk combustion calculation based on realistic decomposition

The realistic decomposition leads to the production of 63.37% gases, 8.69% tar, and 27.94% char. The gases are dominated by H_2O , CO_2 , and CO while the major component of tar is $\text{C}_{10}\text{H}_{14}\text{O}_2$. Water is not produced from moisture but molecule decomposition, known as chemical water. These gases, tar, and char are then oxidized by 100% excess air (1156.94 kg/h) to produce 1276.06 kg/h of flue gas with the composition of 13.69% CO_2 , 4.79% H_2O , 0.20% NO , 70.60% N_2 , and 10.72% remaining O_2 . The specific energy of about 2.6 MJ/kg rice husk is released at flue gas temperature of 700°C with 5% heat loss. The value of this specific energy is still in the range as stated by Chang et al. [6] and also quite similar to the research conducted by Memon et al. [7], but still far lower than Kwofie et al. [8]. This implies that a realistic decomposition approach for rice husk combustion calculation has a reasonable and logical performance.

The excess air in the combustion process could be represented by the O_2 or CO_2 concentration in the flue gas [8]. Usually, the combustor is equipped with O_2 or CO_2 detector which is installed at the outlet pipe to record the concentration in the flue gas. In absence of gas detector, the flue gas could also be analyzed through gas chromatography to ensure the O_2 and CO_2 amount [19]. This calculation is also able to deliver a nomogram (Figure 3) to interpret the relation between O_2 or CO_2 concentration in the flue gas and excess air in the combustion process. Combustion efficiency represents the effective heat utilized in the combustion process where the value becomes lower at a higher excess air and flue gas temperature [20]. The efficiency alleviation due to the higher flue gas temperature is somewhat significant compare to the larger excess air supplied. The nomogram describes that about 10% of O_2 or 9% of CO_2 in the flue gas reflected the 50% of excess air involved in the combustion. In this condition, the combustion efficiency is about 77% at flue gas outlet temperature of 200°C and declining to 21% at outlet temperature of 700°C . When flue gas contains higher oxygen content, let's say 18% of O_2 or 8.2%

of CO₂, it means that the combustion takes place using 100% of excess air. The combustion efficiency is slightly reduced to 74% and 15% at a flue gas outlet temperature of 200°C and 700°C, in a successive term.

Figure 3. Rice husk combustion efficiency nomogram

At higher excess air, substantial nitrogen as an inert gas creates a quenching effect where it absorbs the heat produced and carries it out from the combustor [21, 22]. This impacts on reducing combustion effective heat and lead to low combustion efficiency. Besides that, the higher flue gas temperature at a constant excess air will also lead to poorer combustion efficiency. High flue gas temperature indicates the heat has already flown out from the combustor before it is used for combustion purposes. Accordingly, it is important to utilize the flue gas sensible heat through cogeneration and combine cycle could increase the efficiency [6, 23, 24] although there is a minimum allowable flue gas temperature usually 200°C to prevent flue gas condensation.

3.3. Adiabatic flame temperature (AFT) and air supply strategy for rice husk combustion

Adiabatic flame temperature is the highest theoretical temperature achieved at perfect insulation of the combustion process which is unique for each fuel and only depends on calorific value as long as in absence of molecules

dissociation [25]. AFT is determined through trial error with the assumption of two conditions: perfect insulation condition with no heat loss and 5% heat loss due to radiation. The maximum temperature of this rice husk combustion is calculated up to 1457°C for perfect insulation and this result is slightly lower with the value acquire from Anshar et al. [9]. Again, the realistic decomposition shows its ability to predict the maximal rice husk combustion temperature with a rational result. The negligible discrepancy from another result is strongly caused by different rice husk chemical properties. Subsequently, the heat loss due to radiation will give a quite lower AFT with a discrepancy around 30-60°C as notified in Figure 4.

Figure 4. AFT for rice husk combustion at various excess air

Similar to the previous explanation, larger excess air provides lower AFT. The nitrogen in excess air dilutes and cooled down the flue gas temperature due to the sensible heat absorption [21, 22]. Rice husk combustion is usually maintained at 700°C in order to prevent silica crystalline formation on its ash which could threaten human respiratory systems [26]. To achieve this, the excess air of 200% or air to fuel ratio (AFR) of 17.35 should be supplied for rice husk combustion under perfect insulation of combustor. If there is a 5% heat loss due to radiation, the excess air supply of about 180% or AFR 16.19 is still allowable.

3.4. Flue gas composition analysis

The biomass thermal process through combustion is a complex set of reactions that produces CO, H₂, CO₂, H₂O, NO, N₂, and remaining O₂ [1, 5]. The calculated fugacity coefficient of these gases is 1 for ideal gas and between 0-1 for real gas, which means that there is an intermolecular force attraction [18]. Nevertheless, there is a condition that the fugacity coefficient value is more than 1 which informs that there is an intermolecular force repulsion [16,

18]. The fugacity coefficient for all flue gases is depicted in Figure 5. Calculation with Redlich-Kwong, Soave-Redlich-Kwong, and Peng-Robinson models show slightly similar results. It is also shown that all flue gases have an average fugacity coefficient of nearly 1. The gas acts more ideal at a higher temperature, which is characterized by a fugacity coefficient that is closer to 1 [13, 16]. The fugacity coefficient value is then used for Gibbs Energy minimization calculation to predict the flue gas composition.

Figure 5. Flue gas fugacity coefficient at various temperature

At a temperature of up to 700°C, the complete oxidation of compounds based on C and H atoms are still spontaneous whereas an opposite pattern is found for N atom [2, 13]. In the previous section, NO calculation resulted in 0.20% or 25.4 g NO emission for 1 kg of combusted rice husk (see Figure 2). Meanwhile, thermodynamics calculation reveals that NO (on behalf of the major NO_x compound) has a very low equilibrium constant, 3.88×10^{-4} at 700°C. Moreover, biomass combustion is frequently found at below 1000°C due to the more inferior calorific value than fossil fuel, which leads to the negligence of the NO emission value [2, 17, 27].

On the other hand, CO₂ and H₂O are spontaneously formed and the CO produced from the decomposition will also immediately convert to CO₂. However, the CO complete oxidation is only undergone when air is supplied surpassing its stoichiometric value. Following Le-Chatelier principles, CO oxidation to CO₂ is more favored when more oxygen is supplied [28, 29]. The advantage of providing excess air is clearly to suppress the CO emission. Even though there is still a probability for CO and H₂ to be produced which is caused by the unburnt biomass and CO₂ in the combustor allows Boudouard reaction to occur [28, 30]. The CO produced has a chance to react with H₂O to form H₂ through homogeneous WGSR.

In pursuance of the single reaction simulation, the Boudouard reaction is feasible when the temperature surpassing 500°C. The equilibrium conversion of this reaction is found higher along with the increasing temperature, due to the endothermic reaction. The opposite pattern is found in homogeneous WGSR, which is exothermic and could undergo at a lower temperature [31]. However, the equilibrium conversion decreases at a larger temperature. For simultaneous reaction, WGSR occurs only when the temperature is above 500°C due to the CO compound is produced above this temperature. The equilibrium conversion for both single reactions is shown in Figure 6a and the conversion of the simultaneous reaction is plotted in Figure 6b.

Figure 6. Equilibrium conversion for Boudouard and WGSR: single reaction (a) and simultaneous reaction (b)

The calculated flue gas composition from Figure 2 is then corrected due to the presence of simultaneous Boudouard-WGSR and the values at various temperatures can be seen in Figure 7. This figure informs that the CO production as well as CO₂ consumption from simultaneous Boudouard-WGSR changes from 8.24-27.30% and 19.23-13.71% as the temperature rises from 500-1000°C. Besides that, H₂ production is also intensified from 1.97-4.77% as well as H₂O alleviation from 2.82-0.02% in line with the increasing temperature. A similar pattern is found in the thermodynamics simulation study conducted by Li et al. where CO and H₂ are obtained in higher yield and at the same time CO₂ yield is decreasing as a temperature increase from 700-850°C [32]. This figure also indicates that a high amount of CO could be produced from combustion through Boudouard reaction at above 500°C. This gas is poisonous to humans, so the amount should be suppressed. Again, providing excess air could allow the CO spontaneous reaction with oxygen to form CO₂. Thus, maintaining rice husk combustion temperature below 700°C, apart from suppressing CO and NO production, also prevents the silica phase in ash into crystalline and silica melting [2, 4, 26, 33].

Figure 7. Corrected flue gas composition

4. Conclusion and suggestion

The thermodynamics simulation performance of rice husk combustion has been studied. Under a realistic decomposition approach, rice husk devolatilization produce 63.37% gases, 8.69% tar, and 27.94% char which are then oxidized by 100% excess air to produce flue gas with the composition of 13.69% CO₂, 4.79% H₂O, 0.20% NO, 70.60% N₂, and 10.72% remaining O₂. About 2.6 MJ/kg rice husk is also released at flue gas temperature of 700°C with 5% heat loss. From this study, rice husk with 14.95 MJ/kg of calorific value could achieve the highest theoretical combustion temperature around 1457°C for perfect insulation condition and under 5% heat loss due to radiation could reduce the combustion temperature by about 30-60°C. According to the thermodynamics simulation, NO emission is extremely low as long as the combustion temperature still below 700°C. Besides, CO emission is still possible to exist if the remaining biomass and CO₂ react through simultaneous reactions of Boudouard-WGSR. Although biomass combustion temperature is definitely lower than fossil fuel combustion, maintaining rice husk combustion below 700°C is a necessity in order to suppress CO and NO emissions as well as preventing silica in ash phase change to crystalline which harms humans. Providing excess air of about 180-200% could be an alternative solution for the problems.

Acknowledgment

This study is the beginning part of the doctoral research in Chemical Engineering ITB. Mr. Steven wishing to acknowledge the tuition fee waiver provided by Voucher ITB no. 186/SK/I1.B01/KM/2019. The authors would also thank the Riset Unggulan PT grants for the research funding.

Declarations

Conflict of interest There is no conflict or competing of interest to declare.

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Figures

Figure 1
Rice husk combustion block diagram with DoF analysis

Figure 2
Rice husk combustion calculation based on realistic decomposition

Figure 3

Rice husk combustion efficiency nomogram

Figure 4

AFT for rice husk combustion at various excess air

Figure 5

Flue gas fugacity coefficient at various temperature

Figure 6

Equilibrium conversion for Boudouard and WGSR: single reaction (a) and simultaneous reaction (b)

Figure 7

Corrected flue gas composition

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