

# COMPARISON OF THE GASIFICATION POTENTIAL OF RICE HUSK SAMPLES FROM BRAZIL AND THAILAND

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**RESUMO** – This work aimed at comparing the gasification potential of rice husk samples from Brazil (CAZ1) and Thailand (CAZ2). The pyrolysis step was performed in two pyrolysis reactors under different conditions. The product yields were determined and related to the pyrolysis conditions applied. The biomass and rice husk chars were characterized and overall char combustion and gasification reactivities were measured by thermogravimetry in synthetic air and in CO<sub>2</sub>, respectively. The differences in samples properties play important roles in the thermochemical conversion steps. These differences may reflect local variations of the agricultural growing conditions, as noticed between the two rice husk samples studied, being the Thai rice husk char more reactive than the Brazilian one both in air and CO<sub>2</sub> gasification.

## 1. INTRODUÇÃO

Rice husk is an important agroindustrial solid residue both in Brazil and Thailand. Many studies in the literature dealt with the relation between pyrolytic conditions with either char reactivity or char structure during biomass gasification (Pindoria *et al*, 1998; Mansaray and Ghaly, 1999; Mansaray *et al*, 1999; Adánez *et al*, 2001; Biagini *et al*, 2008; Asadullah *et al*, 2009). The parameters studied include heating rate, final temperature, pressure, residence time of volatiles and particle size and distribution (Guerrero *et al.*, 2005; Cousins *et al*, 2006 a, b; Biagini *et al.*, 2008). The char structure affects the subsequent oxidation step given that the pores size and distribution determines the accessibility of the reaction gas to the active sites (Bar-Ziv *et al*, 1998; Arenillas *et al*, 2002). Compared with most bituminous coals, biomass materials present significant amounts of alkali and alkaline earth metallic (AAEM) species (mainly K, Na, Mg and Ca), which tend to volatilise during pyrolysis (and gasification/combustion), being of important consideration in all aspects of biomass thermochemical conversion. When retained in char during pyrolysis, are important catalysts for the gasification/combustion of char (Raveendran and Ganesh, 1998; Zolin *et al*, 2001), helping to reduce the gasification temperature and increase the overall process efficiency.

## 2. MATERIAL AND METHODS

### 2.1. Biomass characterisation

The Brazilian rice husk sample (CAZ1) was characterised as described below. The characterisation results for the rice husk sample from Thailand (CAZ2) have been provided by the researcher Yatika Somrang and only the results have been reported. CAZ1 and CAZ2 samples were ground and sieved to (106-150)  $\mu\text{m}$  sized particles and dried in a re-circulating air oven at 35 °C for 16 h, stored in small glass bottles in the fridge at approximately 6 °C prior to pyrolysis experiments.

**2.1.1 Proximate and ultimate analyses:** Proximate analysis (moisture (M), volatile matter (VM), ash (A), fixed carbon (FC)) was carried out following DIN 51718 (DIN, 2002), DIN 51720 (DIN, 2001) and DIN 51719 (DIN, 1997), respectively. Ultimate analysis (C, H, N, S, O) was carried out according to the ASTM D3176 method (ASTM, 1997). The oxygen content was calculated by difference. Chloride was measured using selective ion electrodes (Cole-Parmer).

**2.1.2 Heating Value:** The Higher Heating Value (HHV) and the Lower Heating Value (LHV) were determined by applying the methods ASTM D5865 (ASTM, 2004) and DIN 51900 parts 1 and 3 (DIN, 2000; DIN, 2005) to samples previously dried. The HHV was determined in a calorimeter and the LHV was calculated using the Dulong equation (1), with HHV and LHV in  $\text{MJ}\cdot\text{kg}^{-1}$ , H is the mass fraction of hydrogen and M the moisture content of the sample:

$$\text{LHV} = \text{HHV} - 2.43 \cdot (9 \cdot H + M) \quad (1)$$

## 2.2. Biomass pyrolysis

Pyrolysis experiments were carried out in: (1) a horizontal tube furnace (TF) and (2) a hot-rod reactor (HRR), which were described by Virmond (2011). The operating conditions were presented in Table 1. The residence time was previously tested and 900 s was the minimum necessary to promote complete devolatilisation of the sample at the temperatures evaluated.

Table 1 – Conditions applied to the pyrolysis experiments with CAZ1 and CAZ2

	PS <sup>a</sup> [ $\mu\text{m}$ ]	T <sup>b</sup> [°C]	HR <sup>c</sup> [°C.s <sup>-1</sup> ]	t <sub>r</sub> <sup>d</sup> [s]	Gas <sup>e</sup>	p <sup>f</sup> [bar]	v <sub>s</sub> <sup>g</sup> [m.s <sup>-1</sup> ]
<i>Tube furnace</i>							
CAZ1	(106-150)	350, 500, 700, 850	0.8	900	N <sub>2</sub>	1.0	0.1
CAZ2	(106-150)	350, 500, 700, 850	0.8	900	N <sub>2</sub>	1.0	0.1
<i>Hot-rod reactor</i>							
CAZ1	(106-150)	500	1	900	He	2.2	0.1
CAZ2	(106-150)	500	1	900	He	2.2	0.1

<sup>a</sup> Particle size; <sup>b</sup> Pyrolysis temperature; <sup>c</sup> Heating rate; <sup>d</sup> Residence time at the pyrolysis temperature; <sup>e</sup> Carrier gas; <sup>f</sup> Pressure inside the reactor; <sup>g</sup> Superficial velocity of the carrier gas.

**2.1.1 Pyrolysis in the TF:** A tube furnace (STF Model 16/180, Carbolite) was used. A quartz tube of 10 mm internal diameter, 12 mm outer diameter and 113 cm long was fitted into the ceramic tube of the furnace to serve as a support for the sample holder assembly and to limit the pyrolysis environment for smaller mass samples. Sample mass between 0.085 and 0.200 mg of pre-dried biomass were reacted. Each test was repeated at least twice (the repeatability was tested for one sample/condition in five runs at the same conditions). The spread of the data has been estimated by calculating the standard deviations from the results of multiple tests.

**2.1.2 Pyrolysis in the HRR:** The description of the version of the reactor developed by the

Combustion, Gasification and CO<sub>2</sub> Capture group from the Imperial College London and used in the present study as well as of the reactor operation was given by Dabai *et al.* (2010). The HRR runs have been performed with only the first of two stages, which was connected directly to the tar trap. A flow of inert gas (He) was used to sweep the released volatiles into the tar trap placed in a liquid nitrogen bath so that the volatiles released from the reactor could be condensed and trapped. Each test was repeated 1-2 times. The spread of the data has been estimated by calculating the standard deviations from the results of multiple tests. Gas chromatography device (model Clarus 500, Perkin Elmer, FID/TCD) has been used to characterise and quantify the gas components condensed in the tar trap. A packed Alumina F-1 60/80 column was used for analysis of hydrocarbons and a packed Hayesep N60/80 mesh column for CO<sub>2</sub> determinations. CH<sub>4</sub> and CO could not be efficiently collected in the tar trap. Two online ADC analysers based on infrared detection were used to measure the amount (%) of these gas components. The analysers were previously calibrated with a certified gas mixture (supplied by BOC gases).

## 2.3. Characterisation of the pyrolysis char

**2.3.1 Proximate and elemental composition:** The ultimate analysis (CHN) of CAZ1 and CAZ2 char samples produced in the TF at 500 °C and 850 °C, and in the HRR at 500 °C was carried out according to the ASTM D3176 method (ASTM, 1997). The oxygen content was calculated by difference. The contents of moisture, volatiles and fixed carbon were obtained from the TGA experiments performed for measuring the combustion reactivity in a instrument TGA Q 500 (TA Instruments Inc.), such as described in the following section.

**2.3.2 Char combustion reactivity in synthetic air:** The methodology used by Cousins *et al.* (2006 a, b) has been applied to CAZ1 and CAZ2 char samples produced in the TF and in the HRR at 500 °C. A standard isothermal TGA test using a TGA Q 500 (TA Instruments Inc.) was applied to samples of (1.5-3.0) mg. Analysis steps: (1) equilibrium at 50 °C under N<sub>2</sub>, isotherm for 1 min; (2) heating at 40 °C.min<sup>-1</sup> to 110 °C under N<sub>2</sub> at 40 mL.min<sup>-1</sup> and isotherm for 10 min (moisture content); (3) heating at 40 °C.min<sup>-1</sup> to 500 °C and weight stabilisation (VM content); (4) switch from N<sub>2</sub> to air; (5) hold under previous conditions until at least 50% of the sample had reacted; (6) heating at 20 °C.min<sup>-1</sup> to 850 °C to combust the remaining sample and isotherm for additional 5 min (ash content). Weight losses were recorded continuously and the char conversion (*X*) and char reactivity (*r*) were calculated by applying the equations (2) and (3).

$$X = \left( \frac{m_0 - m}{m_0} \right) \quad (2)$$

$$r = -\frac{1}{m_0} \left( \frac{dm}{dt} \right) \quad (3)$$

Where *r* is the reactivity (given in mg.mg<sup>-1</sup>.min<sup>-1</sup>), *m*<sub>0</sub> is the initial weight of the char sample (daf basis) for the combustion step, *m* is the instantaneous sample mass (daf basis) and (*dm/dt*) is the rate of weight loss. Only single determinations have been reported, being the repeatability of *r* determination ±9% of the value quoted.

**2.3.3 Char gasification reactivity in CO<sub>2</sub>:** The experiments were carried out in a thermogravimetric analyser (model DTG 60, Shimadzu) in CO<sub>2</sub> atmosphere at (850-950) °C with

CAZ1 and CAZ2 ((22-27) mg, (106-150)  $\mu\text{m}$ , moisture content of 8.71 wt% and 9.00 wt%, respectively). The pyrolysis step was performed in the proper thermogravimetric analyser as a step previous to char gasification. Analysis steps: (1) purge with  $\text{N}_2$  at  $100 \text{ mL}\cdot\text{min}^{-1}$  and  $35^\circ\text{C}$  for 60 min; (2) heating at  $50^\circ\text{C}\cdot\text{min}^{-1}$  to  $110^\circ\text{C}$  under  $\text{N}_2$  at  $100 \text{ mL}\cdot\text{min}^{-1}$  and isotherm for 5 min; (3) pyrolysis step: heating at  $50^\circ\text{C}\cdot\text{min}^{-1}$  to  $850^\circ\text{C}$  under  $\text{N}_2$  at  $100 \text{ mL}\cdot\text{min}^{-1}$  and isotherm for 15 min; (4) heating at  $50^\circ\text{C}\cdot\text{min}^{-1}$  up to the reaction temperature ( $837^\circ\text{C}$ ,  $888^\circ\text{C}$ ,  $912^\circ\text{C}$  or  $936^\circ\text{C}$ ) under  $\text{N}_2$  at  $100 \text{ mL}\cdot\text{min}^{-1}$ ; (5) gasification step: swicht from  $\text{N}_2$  to  $\text{CO}_2$  at  $100 \text{ mL}\cdot\text{min}^{-1}$ , with isotherm for 120 min. The comparison of the char samples reactivity in  $\text{CO}_2$  (both prepared at  $850^\circ\text{C}$ ) was only made for the gasification temperature of  $837^\circ\text{C}$  in order to check whether the difference observed for the char reactivity in synthetic air at  $500^\circ\text{C}$  (chars produced at pyrolysis temperature of  $500^\circ\text{C}$ ) also occurred in these conditions. The data aquisition was initiated after the purge step was complete. In order to obtain preliminary information about the  $\text{CO}_2$  gasification potential of CAZ1 char, it has been analysed in the same conditions previously described at three additional gasification temperatures:  $888^\circ\text{C}$ ,  $912^\circ\text{C}$  and  $936^\circ\text{C}$ . The degree of carbon conversion ( $X$ ) and the reactivity ( $r_c$ ) in terms of carbon content for gasification with  $\text{CO}_2$  was determined by applying equations (2) and (3) to the data obtained from TGA runs, being  $m_0$  the initial mass of carbon (determined by elemental analysis) in the char sample,  $m$  the instantaneous mass of carbon in the char sample, and  $dm/dt$  the rate of carbon mass loss. The activation energy ( $E_a$ ) in  $\text{CO}_2$  gasification was calculated by plotting  $\ln r_{c\max}$  as a function of  $(1/T)$  for the Arrhenius equation (4):

$$r_{c\max} = k_0 \cdot \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

Where  $r_{c\max}$  is the maximum reactivity ( $\text{mg}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ ) measured during the gasification of the carbon present in the char sample in a given reaction temperature,  $k_0$  is the pre-exponential factor ( $\text{min}^{-1}$ ),  $E_a$  is the activation energy ( $\text{J}\cdot\text{mol}^{-1}$ ),  $R$  is the gas constant ( $8,314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) and  $T$  the absolute temperature (K). This method is applied to the results obtained under the chemically controlled regime. The transition from the chemical to the diffusion-controlled regime can be detected from the change in the slope on the Arrhenius plot.

**2.3.4 SEM/EDS analysis:** The char samples produced from CAZ1 and CAZ2 in the TF and in the HRR at  $500^\circ\text{C}$  were analysed using a Scanning Electron Microscope (SEM) (model TM-1000, Hitachi) equipped with an Energy Dispersive X-ray Spectrometer (EDS) (model SwiftED-TM, Hitachi). The char samples produced from CAZ1 and CAZ2 in the TF at  $850^\circ\text{C}$  were analysed using a Scanning Electron Microscope (SEM) (model EDAX DX-4/EDS, Phillips).

**2.3.5 Trace elements analysis:** Cu, Mg, Mn, Be, Co, Mo, V, Cr, As, Cd, Ni and Zn in the char samples have been quantified by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) after digestion by nitric acid in a closed bomb within a microwave oven in order to investigate possible catalytic effects on the char reactivity. Details of trace element quantification have been presented elsewhere (Richaud *et al.*, 1998; Richaud *et al.*, 2000; George *et al.*, 2008).

### 3. RESULTS AND DISCUSSION

#### 3.1. Biomass properties

Table 2 – Biomass properties

Biomass	CAZ1	CAZ2
<i>Proximate analysis</i>		
A <sup>a</sup> (% db <sup>b</sup> )	13.43	16.80
VM <sup>c</sup> (% daf <sup>d</sup> )	76.19	77.54
FC <sup>e</sup> (% daf)	23.81	22.46
M <sup>f</sup> (% ar <sup>g</sup> )	6.89	10.10
<i>Ultimate analysis</i>		
C (% daf)	43.14	46.98
H (% daf)	5.57	5.86
N (% daf)	0.36	0.80
S (% daf)	<0.01 <sup>h</sup>	0.05
O <sup>i</sup> (% daf)	50.91	45.95
Cl (% daf)	0.02	0.36
<i>Heating value (MJ.kg<sup>-1</sup>)</i>		
HHV <sup>j</sup> (daf)	19.06	19.93
LHV <sup>k</sup> (daf)	17.59	17.79

<sup>a</sup> Ash; <sup>b</sup> Dry basis; <sup>c</sup> Volatile matter; <sup>d</sup> Dry and ash free basis; <sup>e</sup> Fixed carbon; <sup>f</sup> Moisture; <sup>g</sup> As received; <sup>h</sup> Not quantifiable, lower limit of quantification equal to 0.01%; <sup>i</sup> Value obtained by difference; <sup>j</sup> Higher heating value; <sup>k</sup> Lower heating value.

### 3.2. Pyrolysis experiments

The pyrolysis experiments at 500 °C in the TF presented the best results in terms of low char yield comparatively to the other temperatures tested. CAZ2 produced a relatively low amount of tar and a relatively high amount of volatiles in the HRR, which implies that it may be the most promising feed of the suite tested as a gasification feedstock. Venderbosch and Prins (2010) discussed the effects of ash properties on biomass pyrolysis, suggesting that high ash content favours charring reactions, which increases char yield. CAZ1 and CAZ2 contained 13.43 wt% and 16.80 w% (db) ash, respectively. The order of the amounts of ash corresponds to the amounts of solid residue (char and ash) produced. Hence it appears that the larger the amount of ash, the larger the amount of char produced. However, as the ash content increases, the C content falls so that the quality of the char (in terms of energy content) falls. Therefore, although a high ash content sample produces more char, the quality of the char produced may not be very good. The total amount of recovered products (tar and chars) was higher than 61% of the original biomass for the two rice husk samples. Comparison with the char yield from the tubular furnace indicates that there was significantly more char remaining when the material was studied in the HRR. This may be due to the higher pressure required in the HRR. The amounts of CH<sub>4</sub>, CO and CO<sub>2</sub> released by CAZ1 (0.2%, 1.4%, 4.0%, respectively) in the HRR at 500 °C were slightly higher than the amounts released by CAZ2 (0.1%, 1.1%, 3.5%, respectively).

### 3.3. Pyrolysis char properties

**3.1.1 Proximate and ultimate composition:** Table 3 presents the results for the samples prepared in the TF and HRR. C, H, N were determined only for the runs at 500 °C and 850 °C.

**3.1.2 Char combustion reactivity in synthetic air:** The maximum combustion reactivity ( $r_{max}$ ) at 500 °C was higher (0.312 mg.mg<sup>-1</sup>.min<sup>-1</sup> for CAZ1 and 0.760 mg.mg<sup>-1</sup>.min<sup>-1</sup> for CAZ2) for the chars produced at 500 °C in the TF compared to the three other pyrolysis temperatures.



Table 3 – Char properties

Biomass	T <sup>a</sup>	M <sup>b</sup>	VM <sup>c</sup>	A <sup>d</sup>	FC <sup>e</sup>	C	H	N
	(°C)	(wt%, db)	(wt%, db)	(wt%, db)	(wt%, db)	(wt%, db)	(wt%, db)	(wt%, db)
<i>Tube furnace</i>								
CAZ1	350	0.66	26.28	26.98	46.74	n.d. <sup>f</sup>	n.d.	n.d.
CAZ1	500	2.15	6.48	40.15	53.37	43.48±0.21	2.58±0.21	0.83±0.07
CAZ1	700	0.32	1.89	46.00	52.11	n.d.	n.d.	n.d.
CAZ1	850	1.13	5.77	46.79	47.44	47.35±0.21	1.72±0.21	0.80±0.07
CAZ2	350	1.16	22.64	31.47	45.99	n.d.	n.d.	n.d.
CAZ2	500	1.22	6.85	42.54	50.62	45.03±0.21	2.57±0.21	0.81±0.07
CAZ2	700	1.74	2.92	46.57	50.52	n.d.	n.d.	n.d.
CAZ2	850	1.05	2.76	47.84	49.40	42.05±0.21	1.45±0.21	0.50±0.07
<i>Hot-rod reactor</i>								
CAZ1	500	3.29	8.78	35.53	55.69	49.48±0.21	2.85±0.21	1.15±0.07
CAZ2	500	3.07	9.60	33.46	56.94	35.58±0.21	2.19±0.21	0.55±0.07

<sup>a</sup> Pyrolysis temperature; <sup>b</sup> Moisture; <sup>c</sup> Volatile matter; <sup>d</sup> Ash; <sup>e</sup> Fixed carbon; <sup>f</sup> Not determined.

The reason for the decrease in char reactivity with the increase in pyrolysis temperature may be due to the increased structural ordering of the carbon matrix, which has the effect of reducing the concentration of reaction sites, such as suggested by Kumar and Gupta (1994). The  $r_{max}$  of CAZ2 was 2-5 times higher than the value found for CAZ1 char at all pyrolysis temperatures in the TF. Comparing CAZ1 and CAZ2 chars produced in the HRR at the same pyrolysis conditions, the  $r_{max}$  was also achieved for the Thai rice husk char, being almost two times higher ( $0.518 \text{ mg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ) than the value found for CAZ1 char ( $0.315 \text{ mg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ). Comparing the two reactors, the  $r_{max}$  of CAZ1 char at 500 °C was similar ( $0.312 \text{ mg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$  for TF, and  $0.315 \text{ mg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$  for HRR). For CAZ2, on the other hand, the  $r_{max}$  of the char produced in the TF was 46.7% higher compared to the one produced in the HRR. According to Ollero *et al.* (2003) and Cetin *et al.* (2004), this can be attributed, in part, to the higher pressure applied during pyrolysis in the HRR (2.2 bar).

**3.1.3 Char gasification reactivity in CO<sub>2</sub>:** The maximum gasification reactivity ( $r_{cmax}$ ) of CAZ2 char ( $0.013 \text{ mg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ) was slightly higher than CAZ1 char ( $0.008 \text{ mg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ), thus confirming the trend observed for reactivity in air at 500 °C. Besides gasification at 837 °C, three other gasification temperatures were applied to CAZ1 char: 888 °C, 912 °C, 936 °C. The total mass loss percentage of approximately 76 wt% was achieved in the pyrolysis step, which corresponds to the VM of CAZ1. The higher conversion was reached at 912 °C ( $X_c=0.57$ ), followed by 888 °C ( $X_c=0.54$ ), 936 °C ( $X_c=0.52$ ) and 837 °C ( $X_c=0.47$ ). However, the reaction rate was higher at 936 °C, being complete in approx. 50 min. As expected, the  $r_{cmax}$  for CAZ1 were essentially dependent on the final heat treatment temperature due to the significant improvement in internal surface area during gasification and/or the catalysis of mineral impurities which become more effective at relatively high temperatures, with higher values occurring at the higher temperature applied (936 °C). It is known that the rate of gasification depends on the accessibility of the reactant gas to the internal surface of porous char where active sites reside. The experimental data was satisfactorily represented by the proposed equations, thus indicating that the reaction kinetics at the temperatures studied were in the chemical reaction control region.  $E_a$  was equal to  $72.91 \text{ kJ} \cdot \text{mol}^{-1}$ , value which is in the range found in the literature ( $70\text{-}220 \text{ kJ} \cdot \text{mol}^{-1}$ ) (Ollero *et al.*, 2003; Feroso *et al.*, 2009; Link *et al.*, 2010). The  $k_0$  obtained was  $24.32 \text{ min}^{-1}$ .

**3.1.4 Trace elements and SEM/EDS analyses:** CAZ1 chars (TF and HRR) contained

particularly high Zn and Ni contents, while the CAZ2 chars (higher values for the combustion reactivity), presented higher concentrations of Cu, probably reflecting local variations of the agricultural growing conditions. Elemental Cu can act as catalyst for clean gasification, either in nitrogen (to yield predominantly CO, CO<sub>2</sub> and hydrocarbons) or in an oxidizing gas. However, alkali and alkaline earth metals such as Na and K, especially Ca, have known catalytic effect on heterogeneous reactions which take place during biomass pyrolysis and gasification processes (Di Blasi *et al.*, 1999). These were found in chars produced in the TF at 500 °C. K was present in higher concentration in CAZ2 char (35.80wt%), 45% higher compared to CAZ1 (19.55wt%), probably responding for the higher CAZ2 reactivity. When CAZ1 and CAZ2 were pyrolysed at 850 °C, the K content decreased (5.51wt% and 5.54wt%, respectively), what suggests that K has volatilised during pyrolysis at 850 °C, reflecting in slightly different values for the maximum gasification reactivity.

## 4. CONCLUSION

The gasification potential of both rice husk samples was verified. The influence of biomass properties and pyrolysis conditions on the char reactivity in both synthetic air and CO<sub>2</sub> indicates that research on pyrolysis technology selection, improvement and optimisation aiming at obtaining products with the required characteristics for gasification has to be extended.

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