Co-Gasification of Rice Production Wastes

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Rice production is one of the major food sources in the world and unavoidably generates large amounts of wastes, mainly husk and straw that must be dealt in an environmentally sound and sustainable way. Traditional solutions, like burning in open fields or soil incorporation, may contribute for local pollution. Even the use of these wastes as animal food is not an appropriate solution. Plastics are also an additional waste arising from the life cycle of rice production, manufacturing and distribution. The co-gasification of these wastes was easily accomplished in a fluidized bed installation using steam mixed with air or oxygen as gasifying and fluidisation agents. By changing the gasifying agent composition it is possible to select the best conditions to co-gasify rice husks and PE wastes blends. For rice husks gasification, highest H_2/hydrocarbons molar ratios were obtained using a mixture of air and steam and an equivalent ratio of 0.2. These conditions correspond to low tar emissions and very good gas yields and gas higher heating values (HHV). Co-gasification of rice husk mixed with PE enables to increase gas HHV, but also generates more tar. Nevertheless using up to 20 % of PE can be considered a promising solution to deal with this kind of wastes. Pollutants like H_2S and NH_3 were formed in the gasification process in acceptable amounts. Co-gasification with PE enables to decrease these pollutants. Depending on the gas end-use, the installation of a hot gas conditioning system could be needed to further decrease the contents of tar, H_2S and NH_3, while also promoting the conversion of hydrocarbons into H_2 and CO.

1. Introduction

Rice production industry is a major food source in the world and thus, the large amounts of wastes that it generates must be treated with low environmental impact technologies to achieve the sustainability of this industry. The main fraction of biomass wastes that are generated are rice husks and straw. These may be burned in open field or incorporated in the soil but these solutions are not long time sustainable and involve large pollutant emissions. During the life cycle of rice production, manufacturing and distribution, plastic wastes, mainly polyethylene (PE) are used. These wastes are difficult to recycle as they may be contaminated from soil contact or from dust.

As there is a growing need for alternative, abundant and renewable energy sources, rice wastes gasification may constitute an attractive solution. The gasification of rice husks is already a studied field, but its co-gasification with other wastes like rice straw and plastics will increase the chances of a more promising energy conversion process, even if it may include its own problems.

Rice wastes present high ash content, rich in silica but also on elements that may decrease the melting point of silica sand used in fluidised beds. On the other hand, plastics present a much higher energetic content per mass and have negligible ash amounts, but originate higher amounts of tar and heavier hydrocarbons. The use of biomass and plastic blends in co-gasification might avoid partially some of the negative effects of each individual waste and thus would improve the gasifier performance.

During the gasification process all the solid wastes reacts with the surrounding atmosphere, which generally contains mixtures of oxygen, nitrogen and steam. There are many reactions that occur, but the main ones include the reforming of hydrocarbons, water-gas shift and partial oxidation (Pinto et al. 2012). The obtained gaseous mixture contains mainly carbon oxides (CO and CO_2), hydrogen (H_2), water vapour and hydrocarbons. The presence of biomass generally promotes the increase of CO production, while PE favours hydrocarbon formation. There are several contaminants and pollutants that may be formed during

the gasification process. Depending on the fuel content in sulphur, nitrogen and halogens like chlorine, several hydrides can be generated in the gasification process, (Pinto et al, 2007b, 2008).

The overall effect of changing some experimental gasification conditions is generally predictable, but the magnitude experienced for each individual fuel blend may not be so straightforward. Thus, it is always required some tests at laboratory scale before some scale up is optimized at a pilot scale, Pinto et al. 2012. One of the more promising innovations for gasification is the use of oxygen instead of air in mixtures with steam. While the diluting effect nitrogen is removed, resulting in a gas with better HHV, tar and other contaminants will be present at higher concentrations, which will require more demanding gas cleaning operations. Replacing air with oxygen in an existing installation will also increase the residence times inside the gasifier, which will cause some changes on the extent of the gasification reactions, resulting in somewhat different gas compositions, (Pinto et al. 2012, Pu et al. 2013).

The experience and knowledge obtained with several biomass species and wastes types were applied to co-gasification of rice husks blended with PE wastes with the aim of producing energy to be used in rice production process.

2. Experimental Part

2.1 Bench-scale gasification experimental installation

The bench-scale installation used for gasification and co-gasification tests is presented in Figure 1. The reactor was made of a refractory steel and was circular in cross-section with an inside diameter of 0.08 m and with a height of 1.5 m.

The reactor feeding system was water cooled to prevent blockage that might be due to pyrolysis and melting of the feedstock, before its entry into the gasifier. A nitrogen flow was also used to help feedstock feeding and to avoid gas back flow. The reactor was a bubbling fluidised bed gasifier. The gasifying/fluidising agent were mixtures of steam and air (or oxygen), which were fed through a gas distributor at the base of the reactor.

The gasification gas went through a cyclone for particulates removal. Tar and condensable liquids were retained in a quenching system. Gas was then filtered and injected into CO and CO_2 on-line analysers. Gasification gas was sampled and collected in bags to be analysed by gas chromatography (GC).
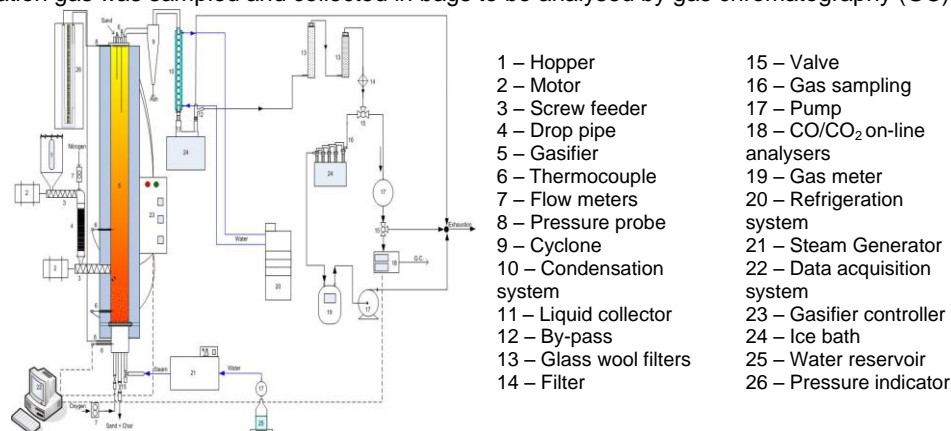

1 – Hopper	15 – Valve
2 – Motor	16 – Gas sampling
3 – Screw feeder	17 – Pump
4 – Drop pipe	18 – CO/CO_2 on-line analysers
5 – Gasifier	19 – Gas meter
6 – Thermocouple	20 – Refrigeration system
7 – Flow meters	21 – Steam Generator
8 – Pressure probe	22 – Data acquisition system
9 – Cyclone	23 – Gasifier controller
10 – Condensation system	24 – Ice bath
11 – Liquid collector	25 – Water reservoir
12 – By-pass	26 – Pressure indicator
13 – Glass wool filters	
14 – Filter	

Figure 1: Schematic diagram of bench-scale fluidised bed gasification installations

2.2 Raw materials and experimental conditions

Ultimate and proximate analysis of rice husk (RH) and polyethylene (PE) wastes used in gasification and co-gasification studies are shown in Table 1. The amount of PE in rice husks mixtures varied between 0 and 30%. As the amount of rice husks produced in the rice production plant is much higher than that of plastic wastes, higher amounts of PE were not tested.

Feedstocks flow rate was around 5g daf/min and it was adjusted to daf (dry and ash free) basis to account for the effect of moisture and ash contents in different feedstocks. As gasification/fluidisation medium, mixtures of air (or oxygen) and steam were used. Gasification temperature varied between 750 and 900ºC to study its effect on gas composition. The effect of steam flow rate was also analysed, by testing steam/biomass ratios from 0 and 1.4. The effect of increasing ER (equivalent ratio), from 0 to 0.3 was also studied. ER is defined as the ratio between the amount of oxygen added and the stoichiometric oxygen needed for complete combustion of the feedstock.

Table 1: Rice husk and PE wastes ultimate (daf) and proximate analysis (as received).

	Rice Husk	PE
Ultimate analysis (% w/w) (daf)		
C	49.2	85.7
H	2.2	14.3
N	0.44	0
S	0.06	0
O	48.1	nd
Proximate analysis (% w/w)	(as received)	
Fixed carbon	14.4	0.1
Volatile matter	60.3	99.8
Ash	16.6	0.1
Moisture	9.5	0.0
HHV (MJ/kg daf)	19.8	46.4

Daf: dried ash free; nd: not detected

2.3 Analytical procedures

The contents of CO, CO_2, H_2, CH_4, N_2, O_2 and C_nH_m (heavier gaseous hydrocarbons with more than one carbon atom) were determined by GC, using two columns in series, a Porapak Q and a molecular sieve and two detectors (TCD and FID). Gas composition is presented on dry basis. Gas yield was calculated based on the production of inert-free gas per weight of dry-ash-free feedstock, without water. Gas higher heating value (HHV) is defined as the gross calorific value of the inert-dry-free gas on a volumetric basis. Energy conversion was determined as the ratio between the energy present in the produced gas and the energy contained in the gasified feedstock.

Tar content in gasification gas was determined using CEN/TS 15439:2006 Standard. Isopropanol (2-propanol) was the solvent used for tar collection. The homogeneous liquid sampled was evaporated under well-defined conditions and the evaporation residue was weighed to calculate the amount of tar in g/Nm^3.

The sulphur released in the form of H_2S was sampled using method 11 of EPA (Environmental Protection Agency). Sulphide was retained in an absorbing solution of $CdSO_4$ and analysed by iodometry. Nitrogen released as NH_3 was determined using the method CTM-027 of EPA. Ammonia was retained in an acidic absorbing solution of H_2SO_4 0.1 N and then analysed potentiometrically with a specific ion electrode.

After each experiment, solid bed residue, containing silica sand, ashes and unconverted carbon, was collected and analysed. Sand was separated from the remaining solids and char content was determined.

Each experiment lasted between 90 and 120 minutes. This time was enough to collect all the samples at stabilised conditions. At least two replicates were done for each experimental test, when deviations higher than 5% were observed, mostly due to oscillations in feeding of solid material, more tests were performed to assure the reproducibility of experimental results to be below 5%.

3. Results and Discussion

Previous gasification studies led to the selection of 850ºC for the gasification temperature, as the increase of this parameter led to a significant decrease of tar contents in the obtained gas, Pinto et al. 2012. The rise of temperature is expected to promote tar conversion into smaller hydrocarbons molecules by cracking reactions, which could further react and be converted into H_2 and CO by steam and CO_2 reforming reactions. The direct conversion of tar into H_2 and CO might also have occurred. Thus, the increase of temperature led to gas enrichment in H_2, while gaseous hydrocarbons contents decreased.

While maintaining a gasification temperature of 850ºC, several gasification conditions were changed to evaluate the effect of their variation in the characteristics of the obtained gas. Figure 2 presents some molar ratios of gaseous components of the gas phase obtained by changing either the solid waste to be gasified (rice husks and its mixtures with PE) or the gasification agent composition (air, steam, steam and air, or steam and oxygen).

The highest H_2/hydrocarbons and H_2/CO ratios were obtained using air and steam mixtures in rice husks gasification. The obtained gas showed to be suitable for several utilisations, though for some of them, tar contents need to be decreased to avoid the problems that may be caused downstream of the gasifier. Comparing results obtained with air and steam mixtures with those corresponding to the use of only one of these components, has shown that steam promotes the enrichment of the gas in hydrogen, while air increased the amount of both CO and CO_2, as can be seen from the decrease of the $H_2/(CO_2+CO)$ molar ratio. These results agree with the values presented by Pu et al (2013) and Campoy et al (2014).
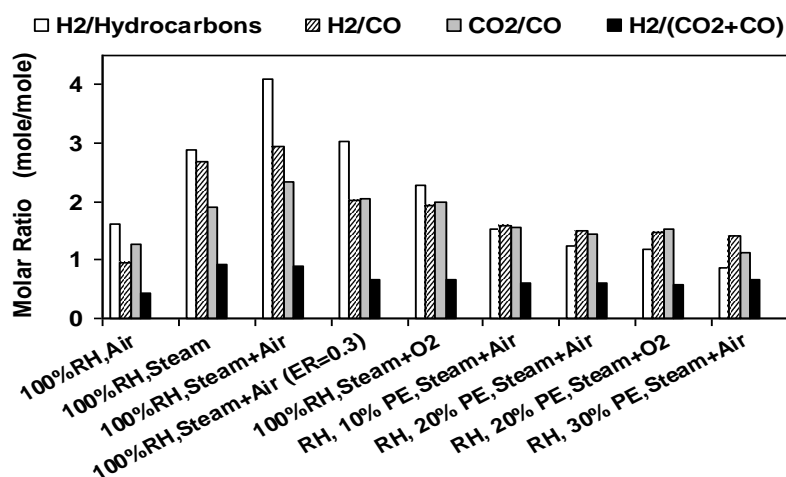
Figure 2: Effect of gasification conditions on gas composition and gaseous molar ratios. When not mentioned otherwise, ER was around 0.2, either in presence of air or oxygen. Gasification temperature was 850 ºC

Co-gasification studies have shown that increases of PE content on the solid waste blend will originate more hydrocarbons corresponding to the decrease of the H_2/hydrocarbon ratio. Accordingly CO_2/CO ratio decreases for higher PE amounts. These results show that PE amounts in biomass blends higher than 30% should be avoided, due to gas enrichment in hydrocarbons and tar, as observed in Figure 3.

The use of steam and oxygen mixtures causes some changes on the obtained gases, namely a decrease on the H_2/CO and H_2/hydrocarbon ratios. This change can be attributed to the higher residence times during the gasification process when oxygen was used, resulting from the lower gas flow rate used when the nitrogen of air was not present. Higher residence times would lead to higher hydrocarbons destruction, however, as tar and char conversion would also be promoted, more hydrocarbons could be formed. This would explain the results observed in Figure 2. In presence of PE, this effect was not observed probably because of the high PE tendency to produce hydrocarbons even at lower residence times.

The selection of the best experimental conditions should also include the evaluation of the parameters presented in in Figure 3. Tar is one of the main contaminants that is formed during the gasification process. It may deposit in the equipment pipes and joints and its accumulation can originate clogging of the installations and higher maintenance and downtime related costs. Lower tar concentrations were obtained while using steam and air, especially for the use of higher ER values. The presence of higher PE amounts on the initial waste mixture caused a large increase of more than fivefold in tar concentrations, due to PE chemical characteristics. The use of oxygen instead of air also originates higher tar concentrations, as in this case there was no diluting effect from nitrogen.

Higher gas yields were obtained using air and steam mixtures as gasification agent. The use of only steam originated the lowest gas production. Replacing air by oxygen decreased the total gas yield, as in presence of air nitrogen was also included. Though higher gas yields were obtained when air was used, the gas produced had lower HHV, mainly due to the diluting effect of nitrogen.

When rice husks were gasified, the highest HHV was obtained with only steam. The presence of 30% of PE also led to a great increase in gas HHV. This was mainly related with the higher amounts of hydrocarbons present in the gas. Changing ER values from 0.2 to 0.3 decreased the gas HHV by more than 13 %. Replacing air by oxygen also increased gas HHV up to 50%, as the diluting effect of nitrogen was absent.

To select some of the best conditions for the co-gasification of rice production wastes a combination of all the opposing effects must be considered. To achieve the highest gas yields, acceptable tar amounts and suitable gas HHV, the best conditions include the gasification of rice husks or its mixtures with up to 20% PE, using air and steam mixtures as gasifying agent. The use of oxygen may also be recommended to increase gas HHV when the gas is intended to be used as fuel.
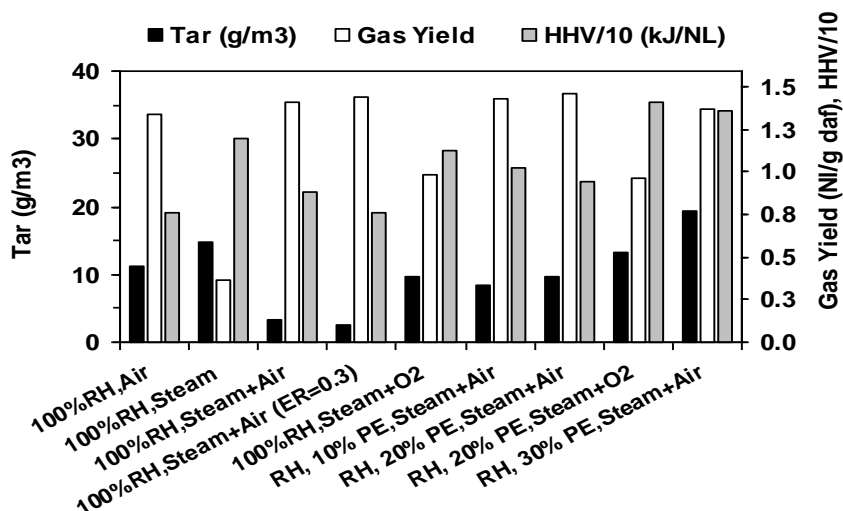
Figure 3: Effect of gasification conditions on gas yield and gas HHV. Experimental conditions were those presented in Figure 2.
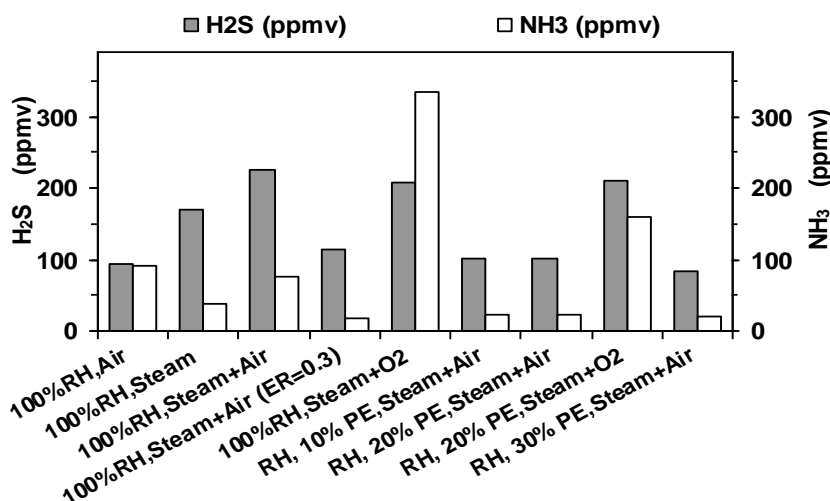

Figure 4: Effect of gasification conditions on the release of H_2S and NH_3. Experimental conditions were those presented in Figure 2

It is also interesting to note that there were small differences on the gas obtained from co-gasification of either 10 or 20% of PE, indicating that PE amount in the blend can be changed among these values when the amount of available PE varies, without negative effects in the gasification process.

In general the results obtained about the effect of PE content on gas yield and composition, including the tar content were in accordance with others found in literature, though other types of feedstock were studied like coal, wastes, sewage sludge or biomass (Pinto et al. 2007a, 2007b, 2008, 2012).

As the wastes used contained some nitrogen and sulphur, as shown in Table 1, their gasification promoted a partial conversion of these elements to pollutants like H_2S and NH_3. The obtained results for H_2S and NH_3 are presented in Figure 4. The amounts of NH_3 were very low as the initial fuels had also low nitrogen contents.

For the case of H_2S in rice husks gasification the highest concentrations were obtained with an ER ratio of 0.2. The presence of PE, further decreased H_2S release, due to the absence of sulphur in PE.

The use of oxygen and steam mixtures as gasification agents led to a large increase in both NH_3 and H_2S, due to the disappearance of the diluting effect of nitrogen from air.

Depending on the gas application, some of tar, H_2S and NH_3 in the gas may be unacceptable. In this case the installation of a hot gas conditioning system could be used to further decrease the contents of these

compounds, while also promoting the reforming of heavier hydrocarbons to hydrogen and CO. Some works related with this catalytic cleaning of the gas can be found in Pinto et al. 2007a, 2007b, 2008, 2012.

4. Conclusions

The gasification of rice husks gasification at a temperature of 850ºC enabled to select a mixture of air and steam and an equivalent ratio of 0.2, as a suitable gasifying agent. These conditions corresponded to the highest H_2/hydrocarbons molar ratios, low tar emissions and very good gas yields and suitable gas higher heating values (HHV).

Co-gasification of mixtures with PE enabled to increase gas HHV, but also generated more tar. However, using up to 20% of PE can be considered a promising solution to deal with these kinds of wastes, as the changes on the gasifying process were acceptable.

The use of oxygen and steam mixtures instead of air and steam, to promote the gasification of rice husks and its co-gasification with 20% PE, generated a gas with higher HHV, which may be useful depending on gas end-use.

Pollutants like H_2S and NH_3 that were formed in the gasification process were detected in acceptable contents. The highest H_2S value was obtained when a mixture of air and steam and an equivalent ratio of 0.2 were used. Co-gasification with PE enabled to decrease partially these pollutants. Gasification tests using oxygen/steam mixtures led to an increase in these pollutants emissions, due to the absence of nitrogen diluting effect.

Depending on the gas end-use, gas treatment in a hot gas catalytic conditioning system could be appropriate to further decrease the contents of tar, H_2S and NH_3, while also promoting the reforming of heavier hydrocarbons to H_2 and CO.

Acknowledgements

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