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# Comparison of Co-gasification of Wastes Mixtures Obtained from Rice Production Wastes Using Air or Oxygen

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The world annual production of rice is higher than 700.7 million tons, which generates rice husk and straw wastes. Rice culture also produces big amounts of polyethylene (PE) bags used in rice packs and for seeds and fertilizer storage that usually end up in landfills, due to their degree of contamination. The energetic valorisation of these wastes may be accomplished by different processes, co-gasification is one of the most viable, as it leads to the production of a synthetic gaseous mixture (bio-syngas) that can be used for energy production to be used during rice milling processes. Gasification of rice husks has some challenges, due to these wastes high content of silica and alkali metals that lead to the formation of solids with lower melting point, thus, leading to bed agglomeration that causes reactor erosion and serious damage. PE has lower ash content and much higher energetic content than rice husks. However, PE polymeric structure may lead to the formation of higher tar contents, which compromise most gasification gas utilisations. Co-gasification of PE and rice husks allows taking advantages of each waste favourable characteristic, diluting the unsuitable

Co-gasification of these wastes was done in presence of steam blended with air or oxygen. Steam promoted the gasification reactions and favoured H<sub>2</sub> production. Air or oxygen promoted the partial oxidation of the feedstocks to be co-gasified and supplied the energy necessary for the endothermic gasification reactions. The use of air has a low cost, but has the great disadvantage of diluting the bio-syngas produced, thus lowering its energetic content. On the other hand, the use of oxygen solves the problems related to gas dilution with nitrogen, but increases the operating cost. Bio-syngas composition obtained by co-gasification trials done with air enriched with different oxygen contents was compared with those obtained with air or pure oxygen to determine the best approach considering both the technical and economical sustainability.

#### 1. Introduction

At present the world faces a critical energy shortage and a global environment concern. Year after year our modern lifestyle demands increasing energy consumption and more other petroleum based products like plastics. Using biomass as a resource to substitute conventional fossil fuels is regarded as one of the most promising approaches to help solving this issue and it is one of the most studied themes nowadays. In the same way, the use of petroleum based plastics is increasing every year worldwide and because of that the great amount of plastic wastes is nowadays a big issue. The most common ways of plastic disposal are through incineration or burying in landfills, which are directly related with several environmental problems (Kim et al., 2011). There are good efforts to recycle plastics, but it is extremely difficult to keep the original characteristics of the virgin polymer after some cycles of recycling (Narobe et al., 2014). In order to pursuit economical and environmental benefits, several technologies like gasification processes have been studied to obtain useful fuels and likewise fossil basic chemicals using plastic and biomass wastes (Kim et al., 2011). Gasification technology is a thermo-chemical process that converts different kinds of feedstock through partial oxidation into a mixture of gases, called syngas, constituted mainly of hydrogen (H2) and carbon monoxide (CO), that together contain around 50% of the energy in the gas product, but syngas also contains methane

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(CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>) and other aliphatic and aromatic hydrocarbons. The most common gasification agents (oxidants) are oxygen (O<sub>2</sub>), steam, CO, air or their mixtures (Bocci et al., 2014, Brachi et al., 2014). The composition of the obtained syngas is directly dependent on the temperature and gasification agent used in the process and the syngas can be used directly as a fuel gas for district heating, electricity production in gas engines and turbines, or in chemical syntheses, for example, Fischer-Tropsch fuels, methanol and platform chemicals (Narobe et al., 2014).

Today, there is a great focus on studying different ways of valorisation of rice husk wastes, the main by-product of rice milling industry with a world annual production of more than 120 million tons (Yoon et al., 2012). Rice husk has a low energy density, high content of silica and alkali metals and consequently it holds a high ash content. Because of this composition, rice husks gasification has some challenges as the formation of solids with lower melting point may lead to bed agglomeration, which may cause serious damage on the reactor (Yoon et al., 2012). Associated with the great production of wastes, rice culture produces great amounts of polyethylene (PE) bags used in rice packs and also for seeds and fertilizer storage that is typically disposed in landfills with several environment issues due to their degree of contamination. PE is a kind of petroleum-based plastic with much lower ash content and much higher energetic content than rice husk. However, PE gasification may lead to the formation of high tar contents, due to its polymeric structure, which can cause several problems in the reactor and compromise most bio-syngas utilizations. To overcome these problems of rice husks and polyethylene plastics, and to take advantage of the specific and favourable characteristics of these two kinds of wastes, the focus of this study is a co-gasification approach using a mixture of PE and rice husks with the aim of diluting the unsuitable features of each material, taking advantages of the favourable ones.

Several studies had shown the success of co-gasification of mixtures of PE with different biomasses. Narobe et al. (2014) studied the volatilization reaction kinetics of 50 wt.% mixtures of PE and wood pellets during gasification processes with a temperature range between 850 °C and 900 °C, comparing with trials with 100 wt.% of PE. These authors came to the conclusion that co-gasification led to successful thermo-chemical conversions of PE as opposed to individual wastes gasification. Another study conducted by Ahmed et al. (2011), focused on the co-gasification of PE and woodchips (WC) mixtures with ratio of PE-WC ranging from 0% to 100%, using steam as gasification agent at the temperature of 900 °C. They concluded that blends of PE-WC when compared to expected weighed average yields from the individual compounds had much better results in terms of syngas, hydrogen, hydrocarbons, energy yields and also thermal efficiency. The best yields were found when mixtures with approximately 60-80% of PE were presented. They also concluded the existence of synergetic interactions between PE and WC during high temperature steam gasification, stating the importance of the input feed composition concluding that small amounts of WC in PE blends resulted in a higher energy yield when compared to sample of 100% PE.

#### 2. Experimental Part

Gasification tests were done in a fluidised bed bench-scale installation, shown in Figure 1. The gasifier was a bubbling gasifier made of a refractory steel pipe. The reactor was circular in cross-section with an inside diameter of 80 mm and with a height of 1 500 mm. The gasifier feeding system was water cooled to prevent some clogging, that might be caused to feedstock pyrolysis, before the entry into the gasifier, especially when PE was used in the feedstock. A nitrogen flow was also used to help the waste feeding. The gasification and fluidisation agent was introduced through a gas distributor at the base of the reactor to act as. The gasification gas formed passed through a cyclone to remove particulates. Tar and condensable liquids were removed in a quenching system. Afterward, the gas was filtered, before it was injected into CO and CO<sub>2</sub> on-line analysers. Gasification gas was sampled and collected in bags to be analysed by gas chromatography (GC) to determine the contents of CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, O<sub>2</sub> and other heavier gaseous hydrocarbons, referred as C<sub>n</sub>H<sub>m</sub>.

Gasification temperature changed in the range of 750 to 900°C. As gasification and fluidisation agent, mixtures of air (or oxygen) and steam were used. Previous studies showed that ER of about 0.2 was a good choice. ER is the ratio between the amount of oxygen added and the stoichiometric oxygen needed for feedstock complete combustion. Feedstock flow rate was adjusted to daf (dry and ash free) basis to account for the effect of moisture and ash contents in different feedstocks. Feedstocks flow rate was around 5gdaf/min. Steam/biomass ratio was around 1.

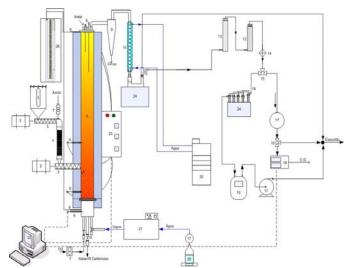


Figure 1: Schematic diagram of bench-scale gasification installation.

Table 1: Ultimate and proximate analysis of rice husk and PE wastes.

Ultimate analysis (% w/w) (daf)	Rice Husk	PE
Carbon	49.2	85.7
Hydrogen	2.2	14.3
Nitrogen	0.44	-
Sulphur	0.06	-
Chlorine	0.08	-
Oxygen	48.0	-
Proximate analysis (% w/w)		
(as received)		
Volatile matter	67.6	99.8
Ash	16.6	0.1
Moisture	9.5	-
Fixed Carbon	6.3	0.1
HHV (MJ/kg daf)	19.8	46.1

Both rice husk and PE wastes were gasified. In Table 1 are presented the ultimate and proximate analysis of these feedstocks. The amount of PE in rice husks blends was varied from 0 to 30%. Higher amounts of PE were not tested, because the amount of rice husks produced in the rice production plant was much higher than that of plastic wastes.

# 3. Results Discussion

No operation problems were observed during gasification rice husk or during co-gasification of rice husk blended with PE. As the production of rice husk during the rice production activities in Portugal is higher than that of PE this study focused first in rice husk gasification and next in co-gasification tests being the amount of rice husk higher than that of PE.

Previous gasification tests showed that gasification temperature was the parameter that most affected rice husk gasification. Thus, it was selected for the comparison of gasification gas composition when air or oxygen was used as gasification medium both blended with steam. As expected, the rise of temperature favoured gasification process by promoting cracking and reforming reactions, thus char produced decreased and gas yield increased with the rise of temperature. As shown in Figure 2, the increase of temperature also led to a decrease in tar content in gasification gas and to an increase in gas HHV (higher heating value). All values presented in Figure 2 refer to the total gas, including  $N_2$  introduced as air. Thus, for air-blown gasification gas HHV were lower than the values obtained when oxygen was used instead of air, because of  $N_2$  diluting effect. With the rise of temperature the difference between gas yields obtained with air and with oxygen tended to decrease, because at higher temperatures more gasification gas was produced.

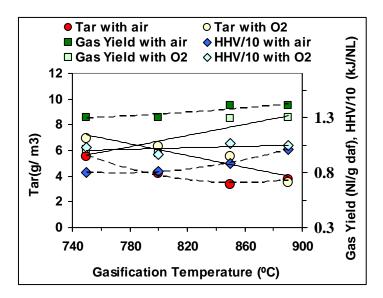


Figure 2: Effect of gasification temperature on tar content, on gas HHV and on gas yield obtained by gasification of 100% of rice husks. Comparison of gasification with air and with  $O_2$ . Gas composition is shown in dry basis. Other experimental conditions: ER - 0.2, steam/feedstock ratio - 1.0.

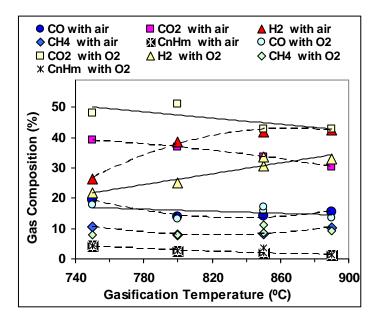


Figure 3: Effect of gasification temperature on gas composition obtained by gasification of 100% of rice husks. Comparison of gasification with air and with  $O_2$ . Gas composition is shown in dry basis and without  $N_2$ . Other experimental conditions: ER – 0.2, steam/feedstock ratio – 1.0.

The real gas composition obtained in presence of air contains around 40 to 50% of  $N_2$ , so the produced gas is  $N_2$  diluted. However, gasification gas composition presented in Figure 3 refers to dry basis and without  $N_2$  to easier the comparison between air-blown and oxygen-blown gasification and also the comparison with data found in literature. Higher temperatures decrease  $CO_2$  and heavier hydrocarbons contents and increased  $H_2$ , because hydrocarbons and tar were converted into CO and  $H_2$  by reforming reactions, Figure 3. However, the evolution of CO and  $CH_4$  was less clear as both compounds were formed and converted during gasification. The same trends were obtained for both oxygen and air blown gasification, though different compositions, due to the differences in inlet gas flow rates, however, ER values were kept around 0.2 for both situations. As shown in Figure 3, the presence of  $O_2$  favoured the formation of  $CO_2$  and decreased  $H_2$ . This effect is more

important for lower temperatures. The contents of all the other gases were similar with air and with  $O_2$ . Best temperature range was  $850-890^{\circ}$ C to which the ratio  $H_2/C_nH_m$  was the highest. The results obtained are in agreement with others referred in literature (Pinto et al. 2008).

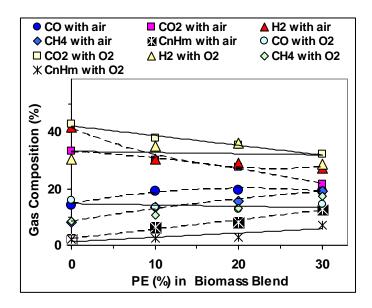


Figure 4: Effect of PE (polyethylene) content on biomass blend on gas composition obtained by co-gasification of rice husks. Comparison of co-gasification with air and with  $O_2$ . Gas composition is shown in dry basis and without  $N_2$ . Other experimental conditions: ER – 0.2, steam/feedstock ratio – 1.0, temperature – 850°C.

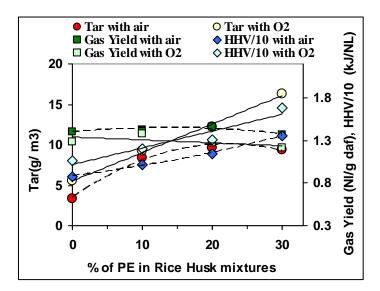


Figure 5: Effect of PE (polyethylene) content on tar content, on gas HHV and on gas yield obtained by cogasification of rice husks. Comparison of co-gasification with air and with  $O_2$ . Gas composition is shown in dry basis and without  $N_2$ . Other experimental conditions: ER - 0.2, steam/feedstock ratio - 1.0, temperature - 850°C.

Air and oxygen blown gasification was also studied for co-gasification of rice husk blended with PE wastes. In Figure 4 gases contents are also presented without  $N_2$ . The same tendencies were obtained in presence of air or  $O_2$ , though different compositions due to the reasons mentioned before. The rise of PE in the blends led to significant increases in hydrocarbons release, while syngas became poorer in  $H_2$ , which agrees with PE polymeric structure. PE amounts higher than 30% (w/w/) were not tested because much higher hydrocarbons and tar contents would be formed and the installation was more difficult to operate and needed more frequent

cleaning procedures. Heavier hydrocarbons were lower in presence of  $O_2$  because of the higher residence times, due to the absence of  $N_2$ , consequently hydrocarbons destruction was favoured, especially at higher temperatures, as hydrocarbons conversion reactions were favoured.

Data presented in Figure 5 refer to total syngas produced, including  $N_2$ , thus lower tar contents were obtained for air-blown gasification, due to the diluting effect of  $N_2$ . With air syngas yields were higher, because of  $N_2$  inclusion. This effect decreased with the rise of temperature, because higher temperatures promoted gasification reaction and the formations of gases. Due to the diluting effect of  $N_2$  lower HHV were also obtained in presence of air. However, in a  $N_2$  free gas basis in presence of  $O_2$ , a gas with lower HHV was obtained, because lower  $O_2$  and hydrocarbons were formed.

#### 4. Conclusions

Co-gasification of rice husk blended with PE wastes was proven to be technological possible, originating a valuable gaseous bio-fuel. The results obtained showed that it is possible to substitute biomass by PE wastes, depending on waste availability. However, the addition of PE needs attention. PE contents higher than 30% should be avoided, because of the high release of tar, hydrocarbons and dust, which difficult the control of the gasifier. This is not a problem as PE wastes produced in rice production activities are in much lower contents than the amounts of rice husk.

The presence of PE led to an increase in tar, in gas yield and in gas HHV, which agrees with the higher contents of hydrocarbons formed by PE polymeric structure. However, the decrease in hydrocarbons content was achieved by increasing temperature, as cracking and reforming reactions were promoted, leading to a syngas richer in  $H_2$  and with lower tar contents. For co-gasification of PE and rice husks blends the selected temperature should be in the range of  $850 - 890^{\circ}$ C, as the highest  $H_2/C_nH_m$  ratio was obtained. To enlarge syngas end-uses, syngas composition may be improved by syngas cleaning and upgrading.

Co-gasification using  $O_2$  instead of air avoided the  $N_2$  diluting effect. Thus, a gas with higher HHV was produced, but at higher operational cost and with higher tar content. Thus the selection of the inlet gasification gas (air or  $O_2$ ) should be done according to the end-use of syngas, as the commercial value of the gas may justify the higher operating cost for its production.

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