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Co-pyrolysis of Wastes Mixtures Obtained from Rice Production. Upgrading of Produced Liquids

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The increasing need to find alternative fuels to decrease the dependency on fossil fuels and to reduce the negative environmental impact of wastes accumulation has led to the idea of studying the energetic valorisation of different types of wastes by co-pyrolysis. Rice production process generates rice husk together with polyethylene (PE) bags that are used for rice packaging and to transport seeds and fertilizers used for rice culture. In Portugal, most of these plastic bags waste usually end up in landfills, since the amount of dirt and dust does not allow their recycling.

Bio-oils produced by rice wastes pyrolysis present some undesirable properties: chemical instability, high solids content, ashes, oxygenated compounds and water, which prevent its direct use in conventional engines. On the other hand, PE pyrolysis produces around 80% w/w of liquid hydrocarbons (bio-oils) composed by a complex mixture of hydrocarbons from C_5 to C_{20} (without the mentioned undesirable properties), 10% w/w of gases and almost no solids. Co-pyrolysis of rice husk blended with plastic wastes leads to the production of bio-oils that may be used as bio-fuels or as raw materials. These bio-oils quality can be improved by the optimisation of co-pyrolysis experimental conditions, including the use of suitable catalysts. Otherwise, liquids may be thermally upgraded to convert heavier liquid molecules into smaller ones with lower molecular weight and better fuel properties. The capability of these bio-fuels for energy production to be used during rice milling processes was analysed. Different approaches: pyrolysis, hydrogenation and pyrolysis followed by hydrogenation were analysed, considering the technical, economical and environmental viability of each process.

1. Introduction

Current global energy production is based on fossil fuels at large extent, through the consumption of huge quantities of non-renewable hydrocarbons at an increasing rate Thus, societies face significant challenges regarding availability of fuels reserves, sustainable use of resources and appropriate management of the wastes produced. The actual framework of fossil fuel markets including insecurity of supplies and political instability has contributed to the development of alternative fuels from different waste materials. Among these materials, biomass and plastic wastes have been commonly approached as a viable alternative to produce a renewable source of new products. Much attention has been given to the valorisation of these wastes through thermochemical conversion processes to decrease the environmental impact of such wastes, by converting them into added value products.

In recent years, there has been a great amount of research in thermochemical conversion processes applied to biomass and plastics mostly due to its efficiency into bio-fuel production (bio-oil, bio-char and bio-gas). Among these processes, pyrolysis has attracted much interest due to the versatility of dealing with a wide range of wastes, including contaminated ones, to produce liquids fuels and chemicals. In addition, advantages regarding storage and transport, and the possibility of use pyrolysis liquids in different applications after processing are not of great concern. However, pyrolysis is still in an early stage of development, mainly due to technical and economic barriers related with traditional fuel production based processes. The production of bio-fuels through pyrolysis has been investigated using different biomasses (Dengyu et al. 2014; John et al.

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2011) and plastics (Pawar et al. 2013; Costa et al. 2007), in different reactors (Asadullah et al. 2007; Aho et al. 2008) as well as in the presence of catalysts (Putun et al. 2006; Muhammad et al. 2012). Other groups of investigators also reported pyrolysis of biomasses mixed with plastics (Bhattacharya et al. 2009; Brebu et al. 2010) including the experimental conditions that were more suitable for maximization of liquids (Pinto et al. 2013; Miranda et al. 2010).

Proper waste selection is a critical issue to be considered when liquid production is of concern. As a result, biomass with high cellulose content is an option as bio-oils are mainly derived from it whilst biomass with low water content is desirable to reduce drying costs and final liquid quality. More recently different groups of researches have published studies concerning the co-pyrolysis of biomass and plastics aiming the production of pyrolysis liquids. Bhattacharya et al. 2009 studied the co-pyrolysis of HDPE mixed with pine wood to produce bio-oils and reported the formation of lower oxygen and water contents, and high heating rates. Brebu et al. 2010 studied the co-pyrolysis of pine cone with synthetic polymers and found that high amounts of liquids products were achieved when compared with theoretical predictions due to possible synergetic effects. In addition, it has been suggested that polyolefinic polymers may provide hydrogen molecules to reactional medium during thermal conversion with biomass leading to an increase of pyrolysis liquids. These studies were carried out focusing the effect of different experimental conditions on pyrolysis liquids yields and properties. However, interactions between biomass and plastic wastes on product distribution and yields remains relatively unexplored mostly with respect to the effect of the thermal degradation of plastics on the decomposition of biomass.

Pyrolysis of these wastes result in the formation of three end products: gas, oil and char, which all have the potential to be used in different applications. The rate and extent of conversion of these wastes into each end-product depend on feed characteristics and ratio as well as on operating conditions. Pyrolysis char is a carbonaceous residue mainly composed of elemental carbon which may result from the thermal decomposition of both organic and unconverted organic compounds. This carbonaceous residue plays an important role in the pyrolysis process since it could contain the mineral content of the waste feed material which may be involved in reactive or catalytic reactions. The gas produced from pyrolysis may be used as a fuel due to the contents of alkanes, alkenes, carbon monoxide and dioxide, hydrocarbons from C1 to C4 and hydrogen. Pyrolysis liquids are a complex mixture of several organic compounds. Pyrolysis bio-oils when produced from biomass may present unsuitable characteristics to be used as fuel including phase separation, instability, ageing and tendency for fouling formation, which may compromise the economic viability of pyrolysis process. Thus, upgraded procedures to improve pyrolysis bio-oils properties are usually needed to enlarge the range of their utilisations. This paper approaches different upgrading techniques of bio-oils produced from co-pyrolysis of rice husk and polyethylene wastes considering technical, economical and environmental aspects. As a result, these wastes were subjected to different processes, as follows: i) pyrolysis in N_2 gaseous medium; ii) hydrogenation; iii) pyrolysis followed by hydrogenation and iv) hydrogenation of pyrolysis liquids. Pyrolysis liquids revealed the presence a vast number of different compounds including alkanes, alkenes, aromatics and oxygenated compounds.

2. Experimental Part

All pyrolysis experiments were carried out in a 1 liter batch reactor of Hastelloy C276 (Parr Instruments). The schematic representation of the pyrolysis setup and all detailed information was published elsewhere, Miranda et al. (2010). Profile of typical curves of reaction temperature and pressure suggested that this is a slow process. This situation occurred mainly due to the high thermal inertia found between the furnace and the interior of the reactor which resulted in average low heating rates of 5 to 6 ºC/min.

Wastes ultimate and proximate analysis is presented in Table1. As mentioned before different processes and treatments were performed. Experimental and analysis procedures were similar to both pyrolysis and hydrogenation processes. Experimental procedure adopted started with loading the reactor with 20% RH mixed with 80% of previously pelletized PE wastes particles of 2-3mm diameter. Then, the reactor was closed and pressurized to a pre-set nitrogen or hydrogen value. Afterwards, the reactor was then heated to a desired temperature and maintained during a reaction time previously established. After this period, the reactor was cooled down to room temperature and opened to retrieve all products. Gases produced during pyrolysis of this wastes were measured and analysed by gas chromatography (GC) to quantify the major components. Liquid fraction directly recovered from the reactor was decanted for liquid separation which was distilled according to standards to yield three additional liquid fractions: i) lighter hydrocarbon fraction with a distillation point lower than 150 ºC, ii) medium hydrocarbon fraction with a distillation range between 150-270 ºC and iii) heavier hydrocarbon fraction with a distillation point higher than 270 ºC. After this temperature was reached, procedure was suspended as the remaining liquid started to degrade which prevent further distillation. Obtained distilled curves were compared to the ones found for standard gas-oil and diesel fuels. Around 70%

volume of pyrolysis liquids were distilled according to standards, though some variations in these volumes were obtained which depend on pyrolysis experimental conditions. The first two distillates were analysed by GC-Hewlett Packard 6890 and GC-MS LECO Pegasus III for compound identification. Solid fraction still soaked in pyrolysis liquid was extracted first with hexane and then with tetrahydrofuran (THF) in a soxhlet extractor according to ASTM D5369-93 and liquids obtained from this process were also analysed in GC and GC-MS equipment.

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

Chapter 2	Rice Husk	PE
Ultimate analysis (% w/w) (daf)		
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

1. Results Discussion

In Figure 1 are presented conversion and products yields obtained by pyrolysis of 20% RH mixed with 80% of PE wastes, as previous studies led to the selection of this composition. Besides pyrolysis under N_2 atmosphere, this mixture was also hydrogenated by different procedures: hydrogenation; pyrolysis followed by hydrogenation and hydrogenation of pyrolysis liquids. The effect of experimental pyrolysis previously studied using the Factoral Design approach showed that the following experimental conditions were a good choice to maximise the production of direct liquid compounds: temperature of 430ºC, initial pressure of 0.2 MPa and reaction time of 10 minutes. These condition were also used for hydrogenation, but a higher hydrogen pressure was also tested, 1MPa. Direct liquid are those easily separated from the solids. Total liquid yields include the direct liquids and those removed from the solids by solvents extraction, using the procedure mentioned before.

Results obtained from pyrolysis and different hydrogenation processes of rice husk blended with PE wastes are presented in Figure 1. No great changes were observed with the increase of initial pressure from 0.2 to 1MPa for both pyrolysis and hydrogenation. Hydrogenation seems to increase both gas and total liquid yields as higher conversions were obtained. The hydrogenation of the liquid and solids obtained by pyrolysis led to a great increase in gas yields, because part of the direct liquids were converted into gases during the second hydrogenation step. The yield of total liquids showed a small decrease, lower than 5% (m/m), which is within experimental error, and may be due to product losses in samples manipulation. Solid yields were similar to those obtained for only one step process, which may suggested that pyrolysis followed by hydrogenation did not lead to further conversion of solids. The small increase observed in conversion was not enough to justify the higher complexity of the overall process. Thus, this option did not seem to be a good one.

The hydrogenation of liquids produced by pyrolysis led to the highest conversion, though this value was only slightly higher than the others. In general, the hydrogenation of liquids led to a better liquids composition, however, a small decrease in total yield was obtained, probably due to some conversion into gases.

Another run was performed; the liquids produced by wastes pyrolysis were separated from the solids and were hydrogenated. No significant improvements were achieved with this approach in relation to products yields and conversion, though a better liquid composition may be achieved. The complexity of performing a two-step process, together with the high operating costs due to H_2 are not favourable features for this option. According to Figure 1 results, hydrogenation of solid wastes may be a valid option.

The effect of the different processes studied on gas composition and properties is shown in Figure 2. As expected, when only pyrolysis was used small amount of hydrogen were found in gas composition when compared with hydrogenation and pyrolysis flowed by hydrogenation. C_nH_m contents achieved the lowest values for hydrogenation processes, which may explain the low values obtained for gas HHV. As a result, hydrogenation processes seems to favour the cracking of higher weight molecules into smaller ones.

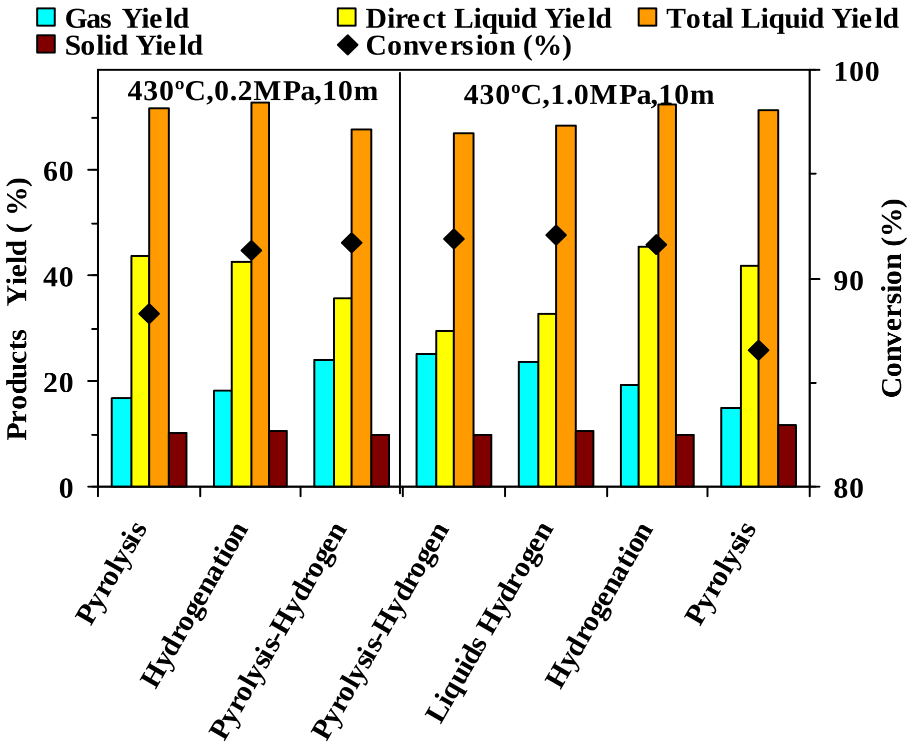

Figure 1: Products yields obtained by pyrolysis and hydrogenation of rice husk blended with PE wastes Comparison between several approaches to obtained liquid compounds.

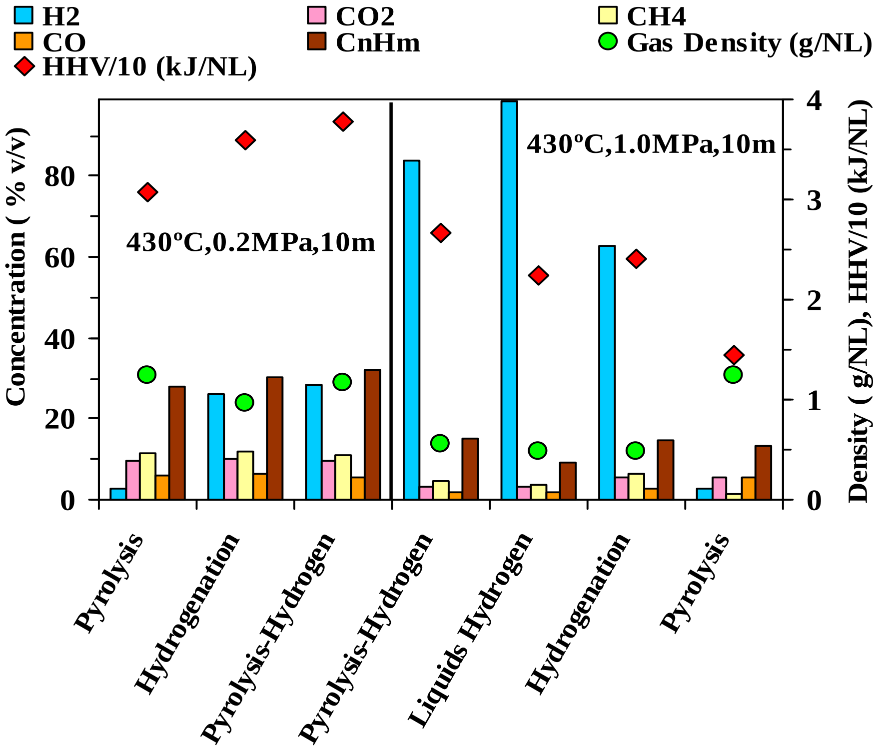

Figure 2: Effect of the process used to convert rice husk blended with PE wastes into liquid compounds on gases composition and properties.

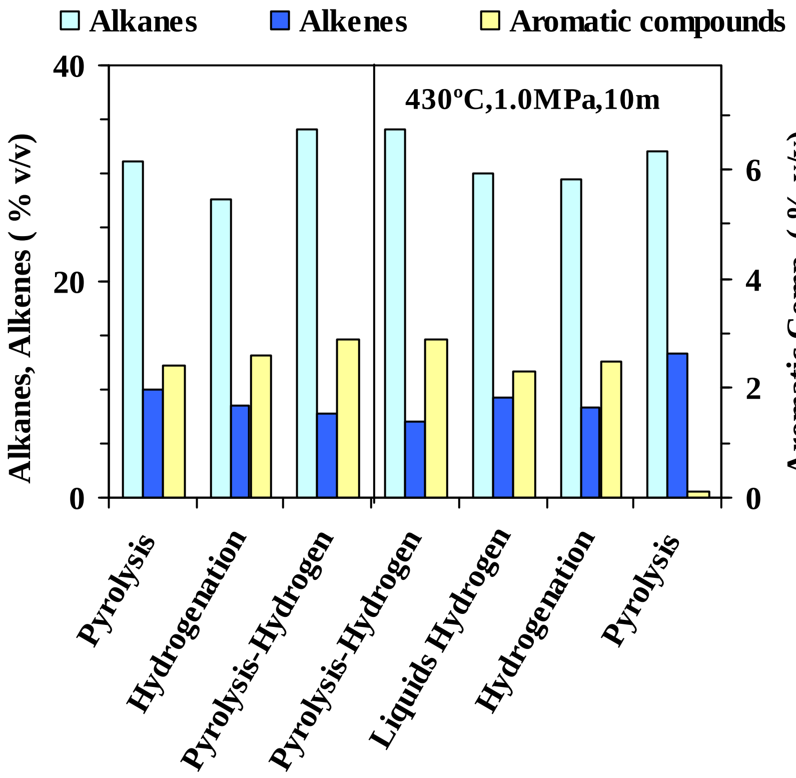

Figure 3: Effect of the process used to convert rice husk blended with PE wastes into liquid compounds on liquids composition.

The analysis of liquids obtained by pyrolysis and hydrogenation processes showed the presence of a large number of different compounds most of them with small contents. Thus, these compounds were grouped in alkanes, alkenes and aromatic compounds and the results obtained are presented in Figure 3. According to the result presented in Figure 3, the highest contents of alkanes and the lowest alkenes were obtained when pyrolysis was followed by hydrogenation of liquids and solids. As more hydrogen was present in the reaction medium double carbon bonds were converted into single ones, thus converting alkenes into alkanes. Alkanes identified range from C_6 to C_{26} being worth mentioning that higher concentrations were obtained for heptane followed by octane, nonane and decane in lesser amounts. Alkenes identified range between C7 to C20 being worth mentioning the formation of octene, nonene and decene. Toluene and ethylbenzene were the aromatic compounds that were identified in higher amounts for all the experiments performed. The addition of hydrogen to the reactional medium, favoured the formation of lighter compounds and when pyrolysis was followed by hydrogenation this process led to great increases in gaseous compounds. This researcher is going on as the liquid compounds need to be further analysed and characterised.

2. Conclusions

It was performed the energetic valorisation of rice husk blended with PE, which are the main wastes found in rice production process in Portugal. PE wastes included bags from rice packaging and transport of seeds. Co-pyrolysis of these wastes resulted in the production of different bio-products (gas, liquid and char). Produced bio-oils and solids were further subjected to different upgrading techniques with gaseous hydrogen. Besides pyrolysis under N_2, those techniques included hydrogenation, pyrolysis followed by hydrogenation and hydrogenation of pyrolysis liquids. Hydrogenation led to higher conversions, as both gas and total liquid yields increased. Pyrolysis followed by hydrogenation was not favourable for further solids conversion and le to great increases of gases. Hydrogenation of liquids resulted in better liquids composition although a small decrease was obtained for total yield probably due to some conversion into gases. Thus, the results obtained by hydrogenation are promising and encourage further research.

Liquids were found to be highly complex and revealed the presence of a vast number of different compounds including alkanes, alkenes, oxygenated and aromatics compounds. Alkanes identified ranged from C_6 to C_{26}

and heptane was found in major concentration. Alkenes were obtained in lesser amounts and compounds between C_7 and C_{20} were identified, the main compounds were octene, nonene and decene. Aromatic compounds were mainly toluene and ethylbenzene. The liquids obtained need to be further analysed and characterised, as the selection of the best process to convert rice husks blended with PE into liquid compounds, depend if these liquids en-uses and commercial value are enough to justify the higher operating costs by the use of hydrogen.

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