

# Study of the Experimental Conditions of the Co-pyrolysis of Rice Husk and Plastic Wastes

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The main objective of this study is to access the technical and economical viability of using pyrolysis technology applied to the rice production main wastes to produce bio-fuels to substitute fossil fuels and electricity consumption during rice milling processes. Therefore, it was studied the effect of operating conditions (reaction temperature, initial pressure and reaction time) on products yields and quality, as well as the possible synergetic effects that may occur during the pyrolysis of these wastes. The pyrolysis experiments were performed in 1 L capacity batch reactor made of Hastelloy C276 and built by Parr Instruments. According to previous studies, the range of operational conditions studied was: 350-430 °C for reaction temperature, 2-10 bar for initial pressure and 10-60 min for reaction time. So far, the results obtained showed that these two wastes can be processed together. The presence of PE seems to favour the biomass conversion, as PE is easily converted into liquids by pyrolysis, which increases heat and mass transfer in the reaction medium.

## 1. Introduction

Modern societies are over dependent on petroleum, being this fuel, the most consumed to produce energy. Hence, efforts have to be undertaken to implement better management solutions of the petroleum resources, both for optimisation of the energy efficiency technologies and also for finding alternative routes for obtaining fuels. This increasing need to find alternative fuels, and also the aim of reducing the negative environmental impact of wastes accumulation has led to the idea of studying the pyrolysis of biomass in the presence of plastic wastes. Rice husk and straw wastes are generated in the rice production process and the polyethylene bags are used to transport seeds and fertilizers and for rice packaging. Biomass and plastics have great potential to provide renewable energy, namely liquid bio-fuels for transportation sector to substitute fossil fuels. The rice husks are a side-product of the rice milling industry, which is produced in large quantities as a waste, approximately 100 million tons of rice husk (RH) are estimated to be produced, annually, in the world. The rice husk is composed of about 78 % of a lignin–cellulose matrix. This biomass has limited applicability as foodstuff for cattle or as power source, so its accumulation is creating an ecological problem, connected to its storage and management (Uzunova et al., 2012).

Rice culture also produces big amount of polyethylene (PE) bags that usually end up in landfills, due to their degree of contamination, since the amount of dirt and dust do not allow their recycling. Pyrolysis is a thermochemical process which has the advantage of allowing the utilization of plastic wastes with contaminants. The Pyrolysis of these two raw materials produces bio-oils that can be used in a wide range of applications, including energy production. PE pyrolysis has been widely studied by several authors (Marcilla et al., 2009; Kaminsky and Zorriquetta, 2007), which have shown that this material can be successfully converted into a liquid hydrocarbon mixture in moderated conditions of pressure and temperature. The pyrolysis of PE can achieve a total conversion of 90 % w/w, being mostly liquid compounds (approximately 80 %), followed by gaseous products (about 10 % w/w) and almost no solid is obtained (Costa et al., 2007). The liquid fraction analysis showed the presence of a complex mixture of hydrocarbons from C<sub>5</sub> to C<sub>20</sub>, in which some of them could be dehydrogenated providing hydrogen to the reaction medium.

Marcilla et al. (2009), studied the thermal degradation of two polyethylene samples (LDPE and HDPE) in a batch reactor and observed that 1-olefins, n-paraffins, dienes and olefins with wide carbon number distributions were the most important compounds obtained in the thermal degradation of both polyethylenes (Marcilla et al., 2009). Polyolefins have a high potential for alternative oil production since they contain only carbon and hydrogen atoms. Kaminsky and Zorriquetta (2007) studied the pyrolysis of polyolefines and concluded that by pyrolysis of these materials up to 95 % of oil and gas can be obtained (Kaminsky and Zorriquetta, 2007).

During the past decade, biomass pyrolysis has been widely studied, especially fast pyrolysis for the production of a liquid product that could be used for combustion, upgraded into diesel oil and gasoline, or to produce chemical raw material (Bridgwater, 2012). Yields of bio-oil as high as 60-75 % based on dry biomass weight can be obtained, depending on experimental conditions used and type of biomass. The composition of the liquid products obtained highly depends on the biomass type and on reaction condition used (temperature, hot vapour residence time, char separation) (Bridgwater, 2012). Some studies using rice husk in the pyrolysis process have been performed, using fast pyrolysis (Yang et al., 2014; Heo et al., 2010; Zheng, 2007). However, these studies showed that the bio-oils produced from rice husk pyrolysis presented undesirable properties, such as chemical instability, high content of water, solids, ashes and oxygenated compounds, which prevent its direct use in thermal devices (Uzunova et al., 2012). These authors studied the slow pyrolysis of rice husk, but with the aim of studying the characteristics of the solid product (Uzunova et al., 2012).

The co-pyrolysis of waste especially plastics with biomass allows to obtain high quality and better quantity of oil in comparison with those obtained from biomass pyrolysis alone (Oyedun et al., 2013). The co-pyrolysis of rice husk and PE wastes was performed with the aim of maximizing the liquid products and improving their characteristics to be used as fuel or raw material for several industries. The presence of PE in the biomass pyrolysis is expected to favour the pyrolysis of rice husk, once the thermal conversion of PE take place at lower temperatures, with the formation of a liquid in the reaction medium that can help the heat transfer, favouring the biomass pyrolysis which, normally, decomposes at higher temperatures.

## 2. Experimental Part

In this study two kinds of wastes, rice husk and PE were used. The rice husk was used as obtained from the rice Portuguese producer. The PE was previously pelletized into particles of 5 mm diameter. The ultimate and proximate analysis of these wastes is presented in Table 1. It was first tested the effect of wastes composition, the amount of rice husks varied between 10 and 50 % and the results obtained showed that the blend with 20 % (w/w) RH and 80 % (w/w) PE allowed to maximise liquid yield. Thus, this blend was selected for the study of experimental conditions effect.

Table 1: Wastes ultimate and proximate analysis (done as received).

Rice husk (RH) and Polyethylene (PE)		
	RH	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)		
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

Authors previous work, (Costa, 2007; Paradela, 2008) has suggested the following range of conditions for process optimisation: run temperature — 350 to 430 °C, reaction time — 10 to 60 minutes, initial pressure — 0.2 to 1 MPa. All the experiments were carried out in an 1 L autoclave (batch reactor), built of Hastelloy C276, by Parr Instruments. The autoclave was first loaded with the waste mixture selected. Afterwards, the autoclave was purged and pressurised to the pre-set value of nitrogen. Then, it was heated and kept at the reaction temperature during the reaction time previously settled. At the end of the pre-fixed reaction time,

the autoclave was cooled down to room temperature and gases were measured, collected and analysed by gas chromatography (GC). Finally, the autoclave was opened and its content was weighted. The liquid products were distilled and three fractions were obtained: one with a distillation point lower than 150 °C, other that distilled between 150 and 270 °C and the liquid residue. The hydrocarbon composition and their content in the two lighter fractions were analysed using a Hewlett Packard 6890 Gas Chromatograph. The quantitative analyse was performed by external calibration using an hydrocarbon standard mixture. The solid fraction were extracted in a Soxhlet extractor, first with n-hexane and then with tetrahydrofuran.

### 3. Results and discussion

In this study was assed the effect of different experimental conditions, reaction time, reaction temperature, and initial pressure for the binary mixture of 20 % (w/w) RH and 80 % (w/w) PE. In Figure 1, 2 and 3 is presented the effect of these experimental conditions in liquid yield. For all the experimental conditions tested, the highest liquid yield obtained was, approximately 74 % (w/w). According to the results obtained, the lowest reaction temperature (350 °C) and reaction time (10 min) led to the formation of the lowest liquid yields, but this value increased from 46 % (w/w) to 51 % (w/w) with the increase of the initial pressure used. These results suggested that both low reaction temperatures and reaction times did not favour the formation of liquids. However, when a higher reaction time (60 min) was used, with the same temperature, the liquid yield reached the highest value of 74 % (w/w). Other than, when for these values of reaction temperature (350 °C) and reaction time (60 min) were used, the increase of initial pressure did not seem to favour the liquid production. For the highest reaction temperature used (430 °C) liquid yields presented similar values, being around 74% (w/w), for both 10 and 30 min reaction time. For the 60 min reaction time this value was always slight lower, especially when the lowest pressure was used. When the highest initial pressure was used, at 430 °C, the values of liquid yield were almost the same, regardless the reaction time used.

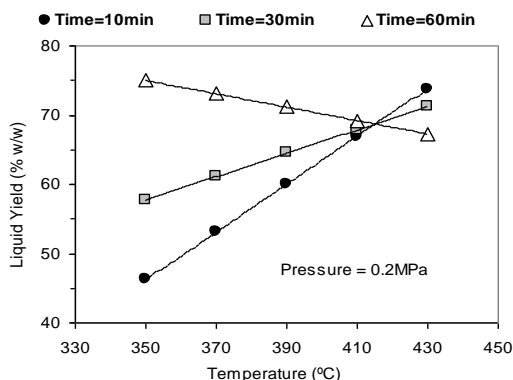


Figure 1: Reaction time effect on liquid yield (Initial pressure of 0.2 MPa)

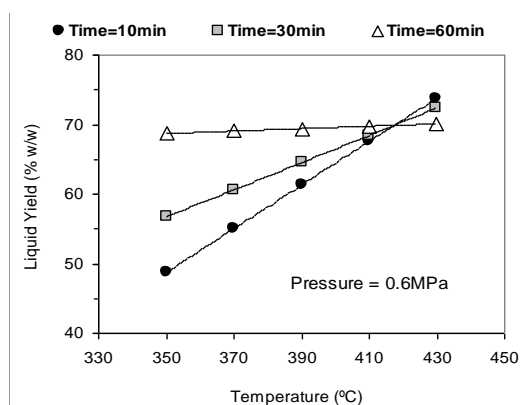


Figure 2: Reaction time effect on liquid yield (Initial pressure of 0.6 MPa)

For the lowest nitrogen initial pressure used (Figure 1), at a constant reaction temperature of 430 °C, the increasing of reaction time seemed to decrease the liquid yields, probably due to an increase in the gas yield.

Maybe, when higher reaction times were used, the carbon bonds could further be cracked to form lighter compounds, which are gases at room temperature. However, for the other two reaction times used, the opposite trend was observed, as the liquid yield raised with the reaction temperature, being the highest value obtained at 430 °C. In fact the liquid yield increased from about 46 % (w/w) to 73 % (w/w) when a reaction time of 10 min was used and from 58 % (w/w) to 71 % (w/w) for the reaction time of 30 min.

For the initial pressure of 0.6 MPa (Figure 2), and for lower reaction times, it was observed a significant increase on liquid yield with the rise of the temperature. This behaviour remained constant until the reaction time of 30 min, but, for higher reaction times, the increase of the temperature does not seemed to affect the liquid yield, once this value was almost constant for all the reaction temperatures used. Probably, the cracking reactions of the heavier molecular into lighter ones, which are liquid at room temperature, take place at lower reaction times, nevertheless the reaction temperature used. At higher pressures, for all the reaction times tested, it was observed a signification increase in the liquid yield with the rise of the temperature, being the highest value obtained at 430 °C. For this temperature a liquid yield of about 74 % (w/w) was observed independently of the reaction time used.

It was also analysed the effect of the experimental conditions in the gas and liquid products composition. For this study it were tested the highest and the lowest experimental conditions used for the same binary mixture (20 % RH and 80 % PE). It was, also tested a mixture with less PE content (70 % w/w). The gas fraction composition is presented in Figure 4. This fraction was mainly composed of hydrogen, carbon monoxide and dioxide and methane. Heavier hydrocarbons were also detected, but in lower concentrations. Higher reaction temperatures and times seemed to favour the hydrocarbon formation, being the highest content of methane (17.4 %) and other hydrocarbon (33.5 %) obtained when 430 °C and 60 min were used. This experimental conditions, also seemed to favour the carbon dioxide formation, reaching its concentration the highest value (9.1 % mol/mol) when 430 °C and 60 min were used. The presence of higher content of rice husk also, seemed to favour the formation of CO<sub>2</sub>. This result can be explained by the presence of the oxygen in the structure of the biomass, what does not happened with PE which is only composed of carbon and hydrogen. The presence of a higher amount of rice husk seems to have increased CO<sub>2</sub> content in the gas fraction.

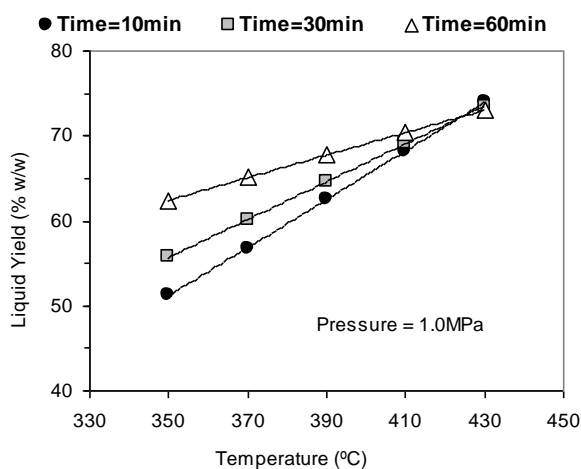


Figure 3: Reaction time effect on liquid yield (Initial pressure of 1.0 MPa)

The liquid fraction which distilled bellows 270 °C was analysed by GC. This fraction was mainly composed by linear alkanes and alkenes with a carbon number between C<sub>5</sub> and C<sub>21</sub> (Figure 5 and 6). The chromatographic profile observed was very similar with the one obtained for the pyrolysis of polyethylene (Costa et al. 2007). Also, Marcilla et al. (2009), observed that 1-olefins, and n-paraffins, with wide carbon number were the most important compounds obtained in the thermal degradation of polyethylene. The alkanes present in higher concentrations, in the liquid pyrolysis product, for all the experimental conditions tested, were between octane and pentadecane, decreasing its content with the increase of the carbon number of the compound (Figure 5). When the lowest temperature (350 °C) was tested the heavier compounds, with carbon number between C<sub>13</sub> and C<sub>21</sub> were detected in higher concentrations. The n-alkanes long chains have better cetane number, so it is favourable to have higher concentrations of these compounds in the liquid product, when it is pretended to use it as fuel for the transport sector. So it is more favourable to use lower reactions temperatures, regarding liquid composition.

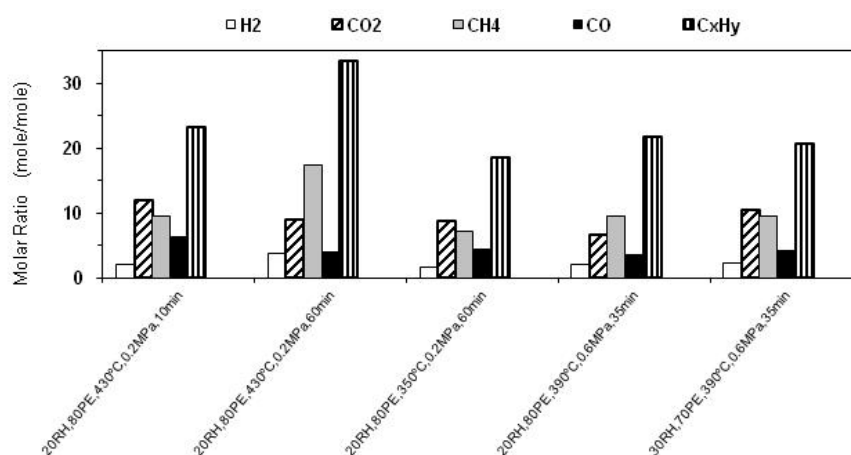


Figure 4: Experimental conditions effect in the gas products composition

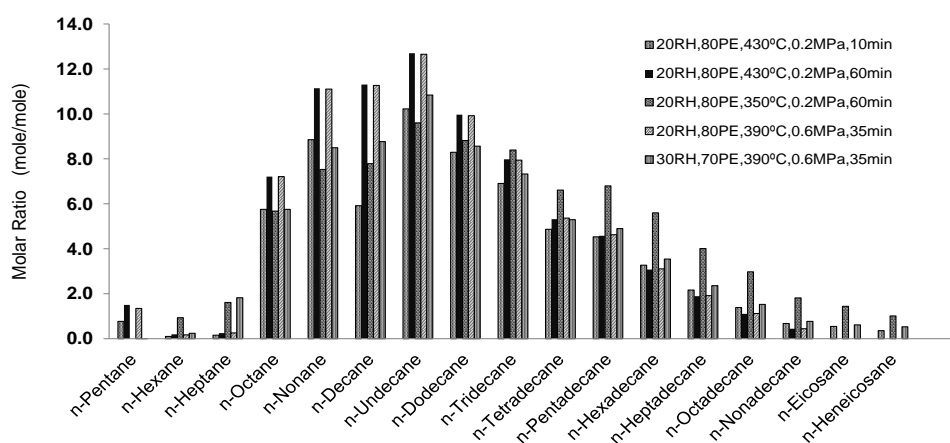


Figure 5: Experimental conditions effect in the linear alkanes formation

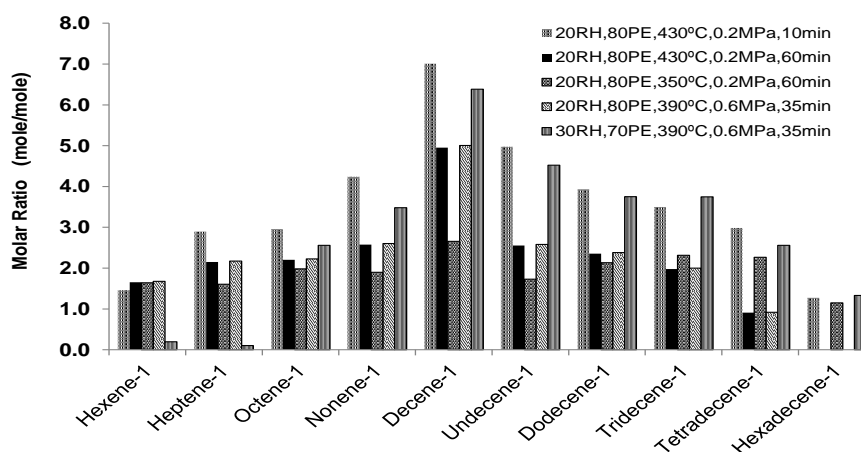


Figure 6: Experimental conditions effect in the linear alkenes formation

These results can be explained by the less energy that is provided to the system that does not allow more extensive cracking reactions to occur. These results were, also, observed by Costa et al. (2008) when performed the kinetic study of polyethylene. When more biomass was used, the changes in the liquid composition were not significant, though liquid yields decreased with the rise of biomass in the blend.

Regarding the alkenes composition, compounds between hexene-1 and hexadecene-1 were detected (Figure 6). The presence of higher content of biomass seemed to favour the production of heavier alkenes. Also, the concentration of alkenes was higher for higher reaction times and temperatures, probably, due to secondary reactions to stabilize the primary radicals formed.

#### 4. Conclusions

The effect of the experimental conditions on rice husk and polyethylene co-pyrolysis products was studied. The lowest reaction temperature (350 °C) and reaction time (10 min) led to the formation of the lowest liquid yields, but this value increased with the rise of the initial pressure used. For higher reaction time, using the same temperature (350 °C), the liquid yield reached the highest value of 74 % (w/w). When the highest temperature was used, the liquid yields presented similar values, being around 74 % (w/w), for reaction times lower than 30 min. For higher reaction times this value was always slight lower, especially when the lowest pressure (0.2 MPa) was used. When higher initial pressure where used, at 430 °C, the reaction time did not seem to influence the liquid yield. For all the experimental conditions tested, the highest liquid yield obtained was, approximately 74 % (w/w). The selected conditions to maximise liquid yields were 430 °C, 0.2 MPa and 10 min or 350 °C, 0.2 MPa, 60 min. Liquid and gaseous products were analysed by GC. The gas fraction was mainly composed by hydrogen, carbon monoxide and dioxide and methane. Heavier hydrocarbons were also detected, but in lower concentrations. Higher reaction temperatures and times seemed to favour hydrocarbon formation. These experimental conditions also seemed to favour carbon dioxide formation. The presence of higher content of rice husk also, appeared to favour the formation of CO<sub>2</sub>. The liquid fraction was composed, mainly, by linear alkanes and alkenes with a carbon number between C<sub>5</sub> and C<sub>21</sub>. The chromatographic profile observed was very similar to the one obtained for the pyrolysis of polyethylene.

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