



Production of liquid hydrocarbons from rice crop wastes mixtures by co-pyrolysis and co-hydropyrolysis



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HIGHLIGHTS

- Co-pyrolysis of rice husk and straw blended with PE (polyethylene) led to liquids with more oxygenated compounds.
- The rise of rice biomass content on PE blends led to an increase in CO and CO₂ in co-pyrolysis gases.
- Study of co-pyrolysis liquids upgrading by hydropyrolysis (with H₂) after co-pyrolysis.
- Co-hydropyrolysis led to the highest conversion and to the highest gas and liquid yields.

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ABSTRACT

The aim of this work was the valorisation of rice crop wastes mixtures by pyrolysis to produce liquids to be used as bio-fuels or as raw bio-materials. The effect of waste mixtures composition on liquids yield and composition was studied. Rice husk (RH) and straw (RS) were pyrolysed with polyethylene (PE), the main plastic used in rice production process. Polypropylene (PP) and polystyrene (PS) were also studied, due to their presence in great amounts in solid wastes. The rise of rice husk amount in PE blends led to a decrease in the conversion of co-pyrolysis (pyrolysis of blends of biomass rice and plastic wastes) and to a reduction of liquid yields. Thus, the blend with 20% (w/w) of rice wastes was selected for further studies. No great changes were observed in the results when husk was replaced by straw, which is advantageous for the pyrolysis process. However, the same was not observed for the type of plastic waste. PS decreased total conversion and the formation of gases and liquids and increased aromatic compounds content in liquids. Some tests were done using hydrogen (hydropyrolysis) instead of nitrogen (pyrolysis) with the aim of improving liquids quality due to the presence of hydrogen in the reaction medium. Different pathways were analysed: (I) co-pyrolysis; (II) co-hydropyrolysis; (III) co-pyrolysis followed by hydropyrolysis and (IV) hydropyrolysis of co-pyrolysis liquids. Co-pyrolysis followed by hydropyrolysis was not favourable for further solids conversion and led to a great increase of gases. Co-hydropyrolysis led to the highest conversion, as both gas and total liquid yields increased.

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1. Introduction

In 2015 the world annual production of rice was higher than 749.1 million tons [1], which generated rice husk and straw wastes. Rice culture also produced a big amount of polyethylene (PE) bags for rice packaging and for seeds and fertilizer storage that usually end up in landfills, due to their degree of contamination. The energetic content of these wastes encouraged the pyrolysis of blends of these two types of wastes (co-pyrolysis) to obtain liquid products to be used as bio-fuels or as raw bio-materials.

Significant research work has been carried out using thermochemical conversion processes applied to different biomass types with the aim of producing a wide range of bio-chemicals and bio-fuels such as bio-oil, bio-gas and bio-char. There has been an increasing interest in studying pyrolysis of rice biomass wastes (husk and/or straw) and a great effort has been put to optimise the pyrolysis process to maximise the productions of liquid bio-fuels [2–18]. Heo et al. [7] studied the effect of different reaction conditions: temperature, flow rate, feed rate, and fluidizing medium on rice husk fast pyrolysis and observed that higher flow rates and feeding rates favoured the formation of bio-oil, being the optimal pyrolysis temperature in the range from 400 to 450 °C. Temperature was the only operation variable that affected the physico-chemical properties of the bio-oil. Naqvi et al. [13] also reported that the pyrolysis

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temperature of 450 °C favoured the production of bio-oil from rice husk pyrolysis. Alvarez et al. [16] stated that bio-oil yield could reach values around 70% (w/w) at 450 °C when a conical spouted bed reactor was used. Qian et al. [17] reported that the rise of pressure from 0.1 MPa to 5.0 MPa promoted the dehydration and decarboxylation of bio-oil, thus, it contained less oxygen and higher calorific value.

Bio-oils obtained from biomass rice wastes pyrolysis may present undesirable properties: chemical instability and high content of solids, ashes, oxygenated compounds and water, which may complicate its direct use in conventional engines [8,9]. Moreover, pyrolysis oil is an unstable product and its physical and chemical properties may change during storage [15]. Besides all this, rice husks pyrolysis has some challenges, due to the high content of silica and alkali metals, which may affect the pyrolysis reactions. Moraes et al. [6] analysed bio-oils obtained by fast pyrolysis of rice husk and reported the presence of five groups of compounds: phenols, ketones, acids, ethers, aldehydes and others. Phenols and ketones were those observed with the highest contents and the major compound was guaiacol. Nevertheless, Ji-lu et al. [10] reported that the bio-oil obtained from rice husk fast pyrolysis at temperatures between 420 °C and 540 °C could be used as a fuel oil for combustion in boilers or furnaces without any upgrading, but for the use in the transport sector some refining was needed. Phan et al. [11] also reported that the bio-oil from pyrolysis of rice straw and husk had the quality to fulfil that of ASTM D7544-12 standard for pyrolysis liquid biofuels. Islam et al. [5] analysed the techno-economic viability of a primary pyrolysis process (FBFP) and of a pyrolysis process with catalytic treatment (FBFPCT) to convert rice husk into pyrolysis oil and reported that FBFP was economically better than FBFPCT for producing primary pyrolysis oil that could be used in boilers.

To improve the production and the quality of bio-oils some authors have tested different catalysts. Zhou et al. [12] observed that in the presence of ZnO bio-oil yields decreased, whilst small molecular compound yields increased. ZnO also decreased the amount of oxygenated compounds and reduced viscosity of the bio-oil. Naqvi et al. [13] also stated that the use of a commercial zeolite ZSM-5 catalyst led to lower yield of bio-oil, but this had higher calorific value and water content. Bakar et al. [3] studied the effect of different catalysts during rice husk pyrolysis and observed that ZSM-5 increased the production of aromatic hydrocarbons and light phenols, whilst Al-MCM-41 decreased the acetic acid production. In general the use of catalysts increased the calorific value and the water content in the bio-oil, whilst its viscosity, density and acid number were reduced. However, the use of a catalyst increases the operational costs of the pyrolysis process.

There is also a huge amount of information about plastics pyrolysis, namely PE [19–26]. Plastics pyrolysis has the advantage of dealing with heterogeneous and contaminated wastes. Around 10% (w/w) of gases and about 80% (w/w) of liquid hydrocarbons may be produced, without the undesirable properties mentioned for biomass pyrolysis liquids [23].

Co-pyrolysis of rice wastes with PE is expected to improve bio-oils quality, as it may allow diluting the unsuitable features of rice wastes and solve the problems related to seasonability. Co-pyrolysis of biomass and polymers has been less studied, though there is some information in literature [27–35]. Bhattacharya et al. [27] reported that bio-oils, obtained by co-pyrolysis of PE mixed with pine wood had low oxygen and water contents. Brebu et al. [28] stated that possible synergetic effects may be found in co-pyrolysis of pine cone with synthetic polymers, as polyolefinic polymers could provide hydrogen molecules that could promote thermal conversion of biomass, thus increasing pyrolysis liquids. By co-pyrolysis the characteristics of pyrolysis oil could be improved and the production cost could be decreased, however, the choice of feedstocks is a key issue [35].

Interactions between biomass and different types of plastics during co-pyrolysis and the effect on product distribution and yields remain relatively unexplored. Co-pyrolysis of rice biomass wastes blended with PE is quite a new subject. Besides PE, polypropylene (PP) and polystyrene (PS) were also studied, as those were the plastic wastes found in greater amount in Portuguese municipal solid wastes. This paper focuses on the production of liquid fuels and/or raw materials through the co-pyrolysis of mixtures of rice biomass wastes and different kinds of plastic wastes.

Besides co-pyrolysis, co-hydrolysis of rice biomass wastes blended with PE was also studied. Hydrolysis uses molecular hydrogen instead of nitrogen, as hydrogen may stabilise the radicals formed by cracking reactions, thus improving liquids quality. Balagurumurthy et al. [36] hydrolysed rice straw and found that with H₂ the bio-oil yield was lower than in presence of N₂. Meesuk et al. [37] also observed a decrease in bio-oil yield in presence of H₂, but the reduction of the oxygen content led to a significant increase in the heating value of bio-oil. Melligan et al. [38] stated that the use of H₂ and its pressure had an important effect in the production of saturated hydrocarbons from hydrolysis of *Miscanthus × giganteus*.

In this paper different approaches were analysed: (I) co-pyrolysis (in N₂ atmosphere medium); (II) co-hydrolysis (in H₂ medium); (III) co-pyrolysis followed by co-hydrolysis and (IV) co-hydrolysis of co-pyrolysis liquids. The aim of the last pathways was to start the cracking process by co-pyrolysis and next add H₂ to further carry on the cracking reactions and mainly to stabilise the radicals initially formed.

2. Experimental part

2.1. Experimental installation and procedure

Co-pyrolysis and co-hydrolysis experiments were carried out in a 1 dm³ volume batch reactor, built of Hastelloy C276 by Parr Instruments, as described elsewhere [39]. Profile of typical curves of reaction temperature and pressure suggested that this is a slow process, as average low heating rates of 5–6 °C/min were found. Experimental and analysis procedures were similar to both co-pyrolysis and co-hydrolysis processes. Experimental procedure started with loading the reactor with the feedstock to be tested. After this, the reactor was pressurised to a pre-set N₂ or H₂ value, heated to a desired temperature and then maintained at it during the reaction time previously established. Afterwards, the reactor was cooled down to room temperature and opened to recover all products.

In Fig. 1 is presented the analysis route of products obtained by co-pyrolysis or co-hydrolysis. Gaseous compounds were analysed by gas chromatography (GC) to quantify the major components. A gas chromatograph Agilent/HP GC6890 equipped with a gas sampling valve, two filling columns and two detectors mounted in series were used. A Molecular Sieve 5A column was used for the determination of nitrogen (N₂), hydrogen (H₂), methane (CH₄), carbon monoxide (CO) and carbon dioxide (CO₂), which were analysed by Thermal Conductivity Detector (TCD). A Porapak Q column was used for the quantification of hydrocarbons in the range C₂ to C₅ which were analysed by flame ionization detector (FID). Argon was used as the mobile phase of both columns. The gas chromatograph was calibrated using standard gas mixtures, whose composition ranges were selected according to the compositions obtained by the co-pyrolysis and co-hydrolysis processes.

Liquid fraction directly recovered was decanted for liquid separation and then distilled according to ASTM D86 standard [40] to

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