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Co-pyrolysis-reforming of Biomass and Residues from Waste Polymer Pyrolysis for CO_2 Reduction and Syngas Enhancement

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The long term utilization of plastic wastes has an important environmental aspect. There is a great effort to waste polymer re-using, recycling and utilization. Chemical recycling can be an attractive possibility for waste polymer recycling not only from environmental, but also from energetic aspects. Especially the possibility for the energetic utilization is widely investigated. The product yield and structure are significantly affected by the process layout and parameters. The further utilization of the gases and pyrolysis oil are well investigated, however there are many unsolved questions regarding the residue. In this article, the value added utilization of waste derived heavy oil was investigated, emphasizing the increasing of the hydrogen content in the liquid hydrocarbons. Raw materials had been pyrolyzed in a horizontal tubular reactor at 550 °C, then the pyrolysis heavy oil were further treated to obtain valuable fractions with high hydrogen content. The results have shown that the re-using of waste derived heavy oil can increase the yield of volatiles, supporting the rearrangement of the molecules to rich favourable product.

1. Introduction

In the past few years, the permanent decrement of fossil fuels has led to a higher claim of renewable energy sources. Besides, the limited availability of fossil fuels, like coal, crude oil and natural gas, the negative effects on the environment are constantly growing. The CO_2 and other pollutants e.g. SO_2, NO_x, CO and hydrocarbons, which are occurred during the ignition of fossil fuels, cause massive environmental problems (Supramono and Lusiani, 2017). Due to the mentioned issues, the use of biomass could be a perspective solution, with its positive effects, eco-friendly nature and as a carbon-neutral source, only having one drawback, the seasonality which can be handled in most cases (Fan and Klemeš, 2020). Various amounts and several types of biomass exist (agricultural, woody, sewage sludge, food industry, animal), considering its availability. In the future, biomass with high organic content e.g. cellulose, hemicellulose, lignin, could be the most used energy source which can be easily converted to bio-gas, bio-oil and heavy residue, depending on the utilized technology (Ahtikoski et al., 2008).

Pyrolysis is an environmentally friendly and efficient process providing an opportunity to produce alternative fuels, chemicals and high purity hydrogen from biomass or polymer waste (Zhang et al., 2018). The pyrolysis can be slow or fast, having a great popularity by the latter one. It is worth to be mentioned, value-added conversion of biomass and polymer waste can be a perspective way regarding the recycling of polymers and biomass, promoted by the catalytic fast pyrolysis (Lin et al., 2015). The H/C ratio and the energy content of the products can be increased by the presence of catalysts. Metal-oxides, molecule sieves, transition metals and zeolites are the most used catalysts, ensuring the stability and the appropriate composition of the products (Bridgwater et al., 2012).

The catalytic fast pyrolysis could be divided into the in-situ improving, meaning the mixture of biomass and catalyst is pyrolyzed, where the reactive solid material and the heat transferer is the catalyst providing quality and property improved products, as well as the ex-situ or "stepwise" improving, where the arising vapors are led

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through a segregated catalyst bed. The ex-situ way could be utilized in a two-stage or a sequenced reactor, having various advantages that could make the thermal and the catalytic steps available at different temperatures. Due to this benefit, the yields and the composition could be easily followed (Iliopoulou et al., 2019).

Simplicity and effectiveness are highly important in developing ideal techniques for the production of synthetic fuels. The quality improvement of the products is promoted by the co-pyrolysis of biomass with different types of materials (Abnisa et al., 2014). During the co-pyrolysis, two or more diverse matters are degrated by the heat, efficiently advancing the basic properties of biomass, pre-eminently the quality and quantity without any modification in the process parameters (Panda et al., 2010).

During the pyrolysis-reformation process of biomass, the yield of hydrogen could be increased by adding plastics or heavy residues into the raw material. With the presence of polyethylene, polypropylene or polystyrene in the raw material, higher gas and hydrogen yield could be obtained owing to polyolefins which are excellent hydrogen sources (Alvarez et al., 2014). Besides, the mentioned materials could be useful in the process of selective production of value-added products (Artetxe et al., 2012). The positive effects on the products can be explained by the better stability of biomass which can improve the radical mechanism of polymer degradation (Brebu et al., 2010). In other words, the degradation temperature of the polymers is decreased, also the interaction is reduced between volatiles and carbon which are formed from biomass (Cornelyssen et al., 2009). Biomass and plastic waste co-pyrolysis is mostly used in case of aiming high stability liquids with low oxygen and large hydrogen content (Pinto et al., 2019). Regarding the obtained heavy oil from waste polymers, there are many challenges with their treatment which is inevitable to be solved in the future. It can be diagnosed, that this kind of measurements have a huge role in recent researches, giving several opportunities to reuse the biomass and plastic waste, also it could be a perspective solution for the heavy oil utilization.

The application of catalysts in gasification reactions is significant, in case of maximizing the hydrogen content (Wu et al., 2013). Nickel (Ni) containing catalysts are widely used during the steam pyrolysis of biomass, due to their low cost and the arising amount of hydrogen in water-shift reaction. Ni catalysts are generally inactivated due to the deposition of carbon (coke) and surface sintering effects at catalytically active sites (Muangrat R. et al 2010). Aluminum-oxide based material (Al_2O_3) is commonly used as a carrier because of its chemical and physical stability and good mechanical properties. Hydrogen and gas yields are also increased with the increasing Ni content in the catalytic system during the pyrolysis oil reformation reactions (Basagiannis and Verykios, 2007).

In our experimental work, pyrolysis-reforming reaction of wheat straw biomass and polyolefin municipal plastic waste based heavy oil mixture was carried out in a two-zoned horizontal tube reactor. As catalyst, (Ni/Al_2O_3) was used in case of quality improvement. The obtained gas and pyrolysis oil was analysed by GC-FID and GC-TCD methods.

2. Material and methods

Municipal polyolefin waste (MPW) (57 % polypropylene and 43 % polyethylene) had been pyrolyzed in a horizontal tubular reactor at 550 °C with feed rate of 5 kg/h (Figure 1).

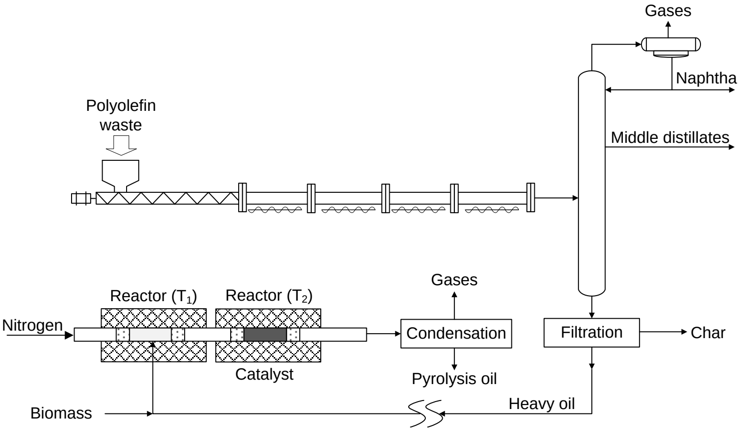


Figure 1: Flowsheet of the used process

Raw material was fed in an extruder and pyrolyzed in a gas heated tubular reactor as the Figure 1 shows. The decomposed products were separated into gases, naptha, middle distillate and heavy oil by atmospheric distillation. After 3 h of stationary operation, 7.1 % hydrocarbon gas product, 29.4 % naphtha, 22.8 % middle distillates, 37.8 % heavy oil and 2.9 % solid char was obtained from the pyrolysis reactor. After the atmospheric distillation, the heavy oil fraction was mixed with wheat straw and pyrolyzed in a two-staged tubular reactor. The main properties of the raw materials (heavy oil and wheat straw) are summarized in Table 1.

Table 1: The main properties of the raw materials

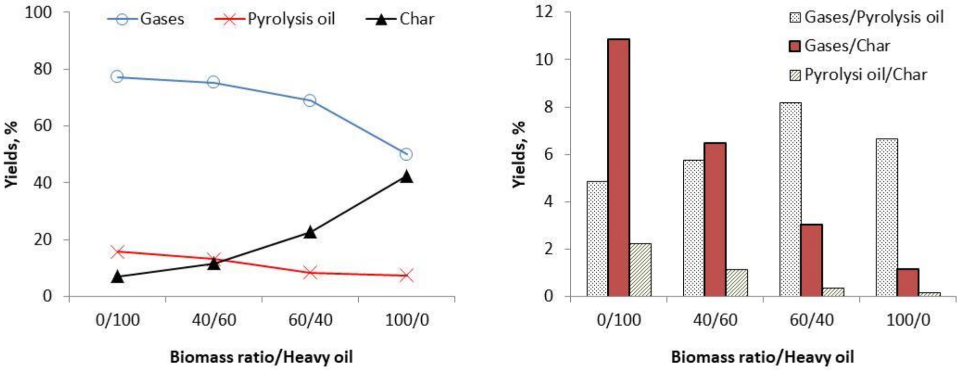
	C	H	N	S	O	Ash, %	Moisture, %	Boiling range, °C	HHW, MJ/kg	Denstiy, g/cm^3
Heavy oil	84.7	15.1	-	0.1	-	0.1	-	>280	44.2	0.916
Wheat straw	42.9	19.8	0.7	0.1	36.5	39.5	7.2	-	18.9	-

At the two-staged tubular reactor 550 °C was used, than the arising volatiles were further treated at 800 °C under nitrogen flow in the presence of structured Ni/Al_2O_3 catalyst (Figure 1). Products from the pyrolysis-reforming tubular reactor were condensed and separated into gases and pyrolysis oil fraction. These different products had been analysed by GC-FID and GC-TCD methods, giving datas about the main components.

3. Results

3.1 Product yields

The yields of products using different heavy oil/biomass ratios are summarized in Figure 2(a), while Figure 2(b) shows the different ratios of products. A perspective solution for heavy oil treating, obtained by pyrolysis was investigated. Regarding the mentioned issue, the main purpose was to produce value-added products with high hydrogen and low CO_2 content, comparing the different ratios of biomass and heavy oil. It can be seen that increment in the proportion of heavy oil fraction, has significantly increased the amount of both gaseous and liquid products. It can be explained with the presence of larger molecules in the heavy oil. Due to this statement, at higher temperature, the larger molecules are decomposed to shorter, gaseous hydrocarbons, with almost 80 % conversion as Figure 2(a) represents.



a) b)

Figure 2: The yields of products (a) and the ratios of product yields (b)

In case of biomass this value is significantly lower owing to the high ash and moisture content. The yield of gas product increased from 50.0 % (100 % biomass) to 77.1 % (100 % heavy oil), while the yield of pyrolysis oil increased from 7.5 % (100 % biomass) to 15.8 % (100 % heavy oil). Regarding the yield of solid char, it can be increased significantly with the increase in biomass content. This was partly due to the high ash content of the biomass as it was mentioned above. Comparing the Figures 2(a) and 2(b), it is clear that the decrease in gas yields as function of biomass content is mainly due to increasing in char yields. The amount of gas products per unit liquid yield can significantly increased with the biomass content and reached a maximum at 60/40 ratio. This was mainly due to the fact that biomass produces more gas products than heavy oil obtained from waste plastics. Another obvious difference is that with the increase in biomass content, the gas yield and liquid yield per unit char decreased significantly in both cases. The reason for this was especially the larger amount of solid char from the biomass. The main reason for the maximum of gas/pyrolysis oil yield at 60/40 heavy oil/biomass ratio was that, at higher biomass ratios, the reactions leading to solid product can significantly increase, which can deteriorate the probability of the reactions resulting gases.

3.2 Gases

The composition of gas products had been studied and demonstrated on Figure 3. The pyrolysis-reforming of heavy oil resulted high amount of C_2-C_6 hydrocarbons, while the gas product contained hydrogen as well. Besides, no amount of CO and CO_2 was observed, due to the composition of the heavy oil. However, the biomass had significant effect on the composition which has appeared in the CO and CO_2 content. Both components of gas product increased with the increasing of biomass content of feedstock. Near the concentration of these components, formation of hydrogen was more dominant in parallel with the biomass content.

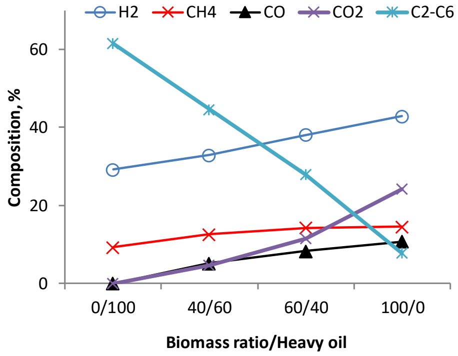


Figure 3: The yields of gas products

As Figure 3 shows, the CO_2 and CO content in case of heavy oil pyrolysis was zero, differently from the values in case of biomass. This phenomena can be explained with the high lignocellulose content of biomass. Owing to the lignocellulose content, which is in connection with the presence of glycosidic-hydroxyl groups, the oxygen content in the gaseous product are significantly higher, presenting more CO and CO_2. Due to the mentioned statements, using a higher ratio of heavy oil, the CO and CO_2 content can be decreased, with the producing of greater yields of larger hydrocarbon molecules. Concentration of syngas components (CO, H_2) increased collectively with the biomass content, while formation of CO_2 was more dominant. CO_2 concentration was 24.2 % during the cracking of biomass. Concentration of methane and C_2-C_6 hydrocarbons decreased significantly due to the increased amount of the biomass in the feedstock. Hydrocarbon composition of gas products are summarized on Figure 4.

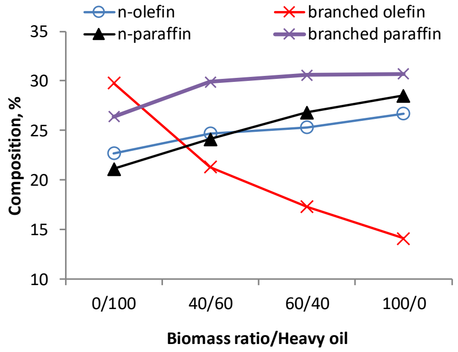


Figure 4: The yields of hydrocarbons in the gas products

Pyrolysis-reforming of heavy oil yielded high amount of branched olefins and significant quantity of branched paraffins. Increasing of biomass concentration in the feedstock resulted more paraffinic product, while the concentration of n-olefins and n-paraffins increased well with the biomass content of the feedstock and the quantity of branched paraffins decreased significantly.

3.3 Pyrolysis oil

The composition of pyrolysis oil can be seen on Figure 5. The concentration of phenol, phenol derivatives and other oxygenated compounds in the pyrolysis oil increased significantly with the increasing of the biomass/heavy oil ratio. This could be explained by the increasing oxygen content in the feedstock which causes higher oxygen content in the liquid products. In accordance with this the n-paraffin and n-olefin content of these products slightly decreased with the increasing biomass ratio of the feedstock.

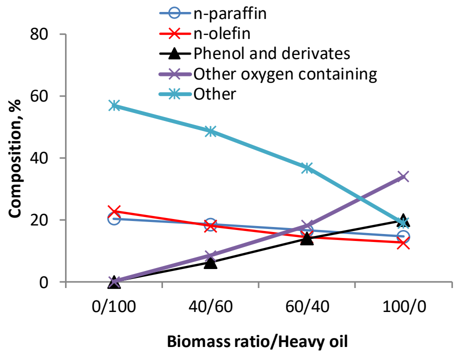


Figure 5: Composition of pyrolysis oils

The aromatic content of the pyrolysis oil products increased with the enhanced biomass/heavy oil ratio as it can be seen on Figure 6.

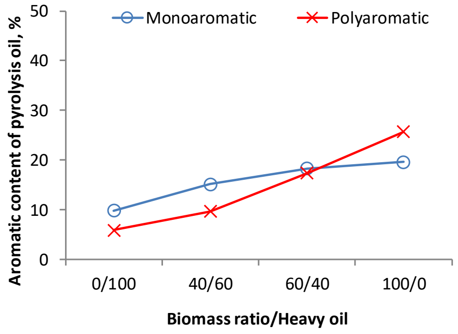


Figure 6: Aromatic content of pyrolysis oils

The incremental monoaromatic content is in accordance with the increasing phenol and phenol derivates content of the pyrolysis oil but the absolute value of it is higher. The significantly higher polyaromatic content of the liquid products can contribute to the elevated char yield since it can be the precursor of the char formation.

4. Conclusions

In this work, biomass and heavy product from municipal polyolefin waste (MPW) pyrolysis were further treated in a two-stage tubular reactor. Catalyst was also used with high nickel content, aiming enhanced hydrogen and lower CO_2 values. The main purpose of the co-pyrolysis is to improve the different properties of biomass, also the quality and stability enrichment of the products. As the results well represent, the higher is the amount of heavy residue in the mixture, the larger yield of the hydrogen, n-olefins, n-paraffins but also the lower amount of C_2-C_6 hydrocarbons and branched olefins. Regarding to the pyrolysis oil, it can be seen that not only the other oxygenated but also the mono-, and polyaromatic compounds have a higher value with the increased biomass content in the raw material, eg.: 25 % polyaromatics and 20 % monoaromatics were observed in case of only using biomass, while 5 % of polyaromatics and 10 % of monoaromatics were formed without biomass content in the raw material. This can be explained with the high oxygen content in the mixture due to the cellulose in the biomass. Regarding the mentioned results, it can be mentioned that high biomass content in the raw material is useful in case of syngas production but it has several drawbacks during the long term utilization of pyrolysis oil. Summarizing the results, it can be established that the heavy oil had positive effects on the composition of the products, also CO_2 reduction and increased hydrogen production were occurred due to the co-pyrolysis. However, a significant question is the use of the observed pyrolysis oil and also, the purification of the gaseous product which should be investigated in the future works.

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