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Hydrochar production through co-hydrothermal carbonization of water hyacinth and plastic waste

M Y Ong[1*], S Nomanbhay[1*], C U A A C Rosman[2], T Yusaf[3,4] and A S Silitonga[5,6]

[1] Institute of Sustainable Energy (ISE), Universiti Tenaga Nasional (UNITEN), 43000, Kajang, Selangor, Malaysia
[2] Department of Mechanical Engineering, College of Engineering, Universiti Tenaga Nasional (UNITEN), 43000, Kajang, Selangor, Malaysia
[3] School of Engineering and Technology, Central Queensland University, Brisbane, QLD 4009, Australia
[4] College of Engineering, Almaaqal University, Basra 61003, Iraq
[5] Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology Sydney, Ultimo, NSW 2007, Australia
[6] Center of Renewable Energy, Department of Mechanical Engineering, Politeknik Negeri Medan, 20155 Medan, Indonesia

*E-mail: me089475@hotmail.com; saifuddin@uniten.edu.my

Abstract. The global expansion of the economy and concerns about greenhouse gas emissions and climate change necessitate the exploration of sustainable alternatives to fossil fuels. Water hyacinth (WH) is globally recognized as one of the most problematic aquatic weeds, posing significant challenges to urban management by clogging waterways, polluting water sources, and causing harm to ecosystems. However, water hyacinth is enriched with hemicellulose, cellulose, and lignin, making it a noteworthy and superior biomass resource. Hence, this study focuses on the hydrothermal carbonization of water hyacinth into a renewable fuel source, the hydrochar. Hydrothermal treatment was implemented in this work as it can treat wet biomass, in this case, the water hyacinth, without the need of energy-extensive drying process. Plastic waste (PW), or more specifically low-density polyethylene (LDPE), was added as the co-feedstock during the HTC process with the purpose to boost the higher heating value (HHV) of the end product. The co-hydrothermal carbonization (co-HTC) process of the mixture of WH and PW at various ratios and temperatures were conducted to investigate the optimal HTC condition for high hydrochar yields. As the result, the highest hydrochar yield of 29.23 wt% was obtained with 12.5% LDPE substitution percentage, at 200 °C after a holding time of 90 min. However, in term of energy recovery efficiency (ER), the highest efficiency (27.28%) was achieved with 12.5% LDPE substitution percentage at 260 °C. The HHV value of the hydrochar produced in this work is in the range of 17.71-24.69 MJ/kg. In summary, the co-HTC of WH and LDPE could definitely be a promising alternative to bridge the gap from solid waste to renewable fuels.

Keywords: Hydrothermal carbonization, Water hyacinth, Plastic waste, Hydrochar, Energy, LDPE

1. Introduction

Energy plays a fundamental role in global socio-economic development and has wide-ranging impacts. The rising energy demand, fossil fuel depletion issues, concern over greenhouse gas emissions, and climate change have intensified discussions regarding the development of a bio-based economy. Biofuels, derived from biomass, are hence introduced as they are considered more environmentally friendly than fossil fuels, offering greener alternatives like biochar, bioethanol, biodiesel, and biokerosene [1]. The US and Brazil are significant bioethanol producers, while biodiesel is gaining recognition as a petrochemical substitute, supported by the US Environmental Protection Agency [2]. Bio-kerosene, derived from sources like palm oil, is also gaining favor [3]. Most country in the world is actively transitioning towards a circular economy, emphasizing renewable energy sources, including wind, wave, geothermal, biomass, and solar technologies. Resource evaluation, suitable technology implementation, and accommodating energy demand are vital in realizing renewable energy systems [4]. Thermochemical conversion processes have been employed to produce biochar and hydrochar from renewable biomass waste. Among the available thermochemical methods, pyrolysis and hydrothermal carbonization (HTC) are key technique for generating bio/hydrochar. HTC, noted for its elimination of pre-drying process and operation at lower temperatures, shows promise as a technology. The parameters, such as feedstock type, reaction temperature, holding time, and *etc.* are linked to the carbon conversion and the yield and quality of hydrochar produced [5].

Water hyacinth, scientifically labeled as *Eichhornia crassipes*, represents a significant threat across multiple aspects of life, encompassing ecosystem functionality, public health, societal progress, and the livelihoods of underprivileged communities. The proliferation of *E. crassipes* has sparked ecological and economic crises marked by diminishing biodiversity and a surge in diseases like filariasis, malaria, dengue fever, and encephalitis among human populations[6,7]. This upsurge is linked to oxygen depletion in regions dominated by water hyacinth, fostering the breeding of snails and mosquitoes, which are key vectors for various diseases. By considering these challenges, there is growing interest in harnessing water hyacinth as a raw material for biofuel production, such as biochar. This approach not only offers a cost-effective strategy for waste management but also contributes to the critical process of carbon sequestration, an area where research regarding water hyacinth control is still lacking [8].

Moreover, plastic waste stands as a significant contributor to environmental contamination and presents mounting challenges in terms of disposal [9]. Plastics, composed of synthetic organic polymers, possess attributes of durability, lightness, adaptability, and cost-effectiveness, rendering them one of the most extensively employed materials worldwide [10]. Nevertheless, the majority of plastics are designed for single-use applications, such as plastic packaging, shopping bags, straws, and disposable utensils, thereby exacerbating environmental pollution. Consequently, a substantial portion of these materials finds their way into landfills, waste sites, open environments, and even oceans, where many petroleum-based plastics exhibit remarkable stability under typical environmental conditions, enduring for centuries or even millennia after disposal. Among these problematic plastic materials, low-density polyethylene (LDPE) emerges as one of the most pervasive culprits in environmental pollution, owing to its widespread use [11]. Hence, in the context of this research, LDPE is specifically chosen as the biomass feedstock. Furthermore, LDPE boasts elevated carbon and hydrogen contents, which significantly bolster the energy value of the end products [12,13].

In summary, this research endeavors to determine the ideal conditions for converting water hyacinth (WH) into biochar using hydrothermal carbonization (HTC), incorporating various proportions of plastic waste, specifically low-density polyethylene (LDPE), as a co-feedstock to enhance the energy content of the final product. The outcomes of this investigation are expected to be of considerable significance to researchers in the realm of sustainable energy, particularly in the field of biofuels.

2. Methodology

2.1. Materials

Water hyacinth (WH) retrieved from the UNITEN reservoirs and low-density polyethylene (LDPE) powder acquired from a neighboring plastic fabrication company are the feedstock used in this work. The WH underwent drying in an oven at 105°C for 24 hours, subsequently pulverized to smaller sizes. Following this, the pulverized WH sample and LDPE powder were individually stored in a sealed bag for use in subsequent experiments.

2.2. Hydrothermal carbonization

The hydrothermal carbonization (HTC) of biomass feedstock was conducted within a hydrothermal stainless steel batch reactor with a volumetric capacity of 1 L, as shown in figure 1. This reactor can withstand high temperatures (up to 350 °C) and pressures (up to 300 bar). Furthermore, it is equipped with a stirrer to ensure the homogeneous mixing of reactants. The HTC process was carried out at specific temperatures (200, 230, and 260°C). Before the experiment, a total sample of 80 g was prepared by mixing WH with 0%, 12.5%, and 25% substitution rate of LDPE, respectively. The water was then added in accordance with a 1:10 biomass-to-water ratio. The prepared sample was then transferred into the batch reactor, which was subsequently closed and sealed using a lifting machine. Before initiating the heating process, the reactor was purged and preloaded with nitrogen (N_2). Subsequently, the overhead stirrer was switched on, and the reaction medium was heated to the desired temperature with a heating rate of 8 °C/min. The temperature was maintained for a duration of 90 minutes. Once the reaction was complete, the reactor was allowed to cool down to room temperature overnight. The liquid and solid products were separated by filtering the mixture through a filter paper under vacuum. The solid product was then placed in a drying oven at 105 °C for at least 16 hours to ensure complete drying. The yield of hydrochar was subsequently calculated using the following equation:

$$\text{Hydrochar yield \%} = \frac{\text{Mass of hydrochar}}{\text{Mass of biomass feedstock}} \times 100\% \tag{1}$$

2.3. Characterization of biomass feedstock and hydrochar

The ash, and moisture content of the feedstock and hydrochar obtained in this work were determined. A known weight of sample was placed in a crucible and dried in an oven at 105 °C [14]. The weight of the sample was measured every 3 hours until constant weight was obtained. The change in the weight was then recorded as the moisture content of the sample. On the other hand, the ash content in the sample was evaluated by burning the oven-dried sample in a furnace at 575 °C for 5 hours 30 minutes [15]. The ash content was calculated using the weight differential before and after the test.

Elemental analysis was performed using a TruSpec-Micro CHNS/O elemental analyzer from Leco Corporation, USA. This analysis determined the composition of carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulfur (S) in the feedstock and the hydrochar produced in this study. The high heating value (HHV) of the biomass feedstock and hydrochar was subsequently calculated using a modified Dulong equation, equations (2) and (3), respectively [16]:

$$\begin{aligned}\mathrm{HHV}_{\text{biomass feedstock}}\left(\frac{\mathrm{kJ}}{\mathrm{kg}}\right) \\ &= 3.55 \times \mathrm{C}^2 - 232 \times \mathrm{C} - 2230 \times \mathrm{H} + 51.2 \times \mathrm{C} \times \mathrm{H} \\ &+ 131 \times \mathrm{N} + 20600\end{aligned} \tag{2}$$

$$\mathrm{HHV_{hydrochar}}\left(\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = 348.11\times \mathrm{C} + 938.05\times \mathrm{H} + 104.60\times \mathrm{S} + 62.76\times \mathrm{N} - 107.95\times \mathrm{O} \quad (3)$$

The energy recovery efficiency was then calculated by using equation (4) [17]:

$$\text{Energy recovery efficiency (\%)} = \text{Hydrochar yield}\times\frac{\mathrm{HHV_{hydrochar}}}{\mathrm{HHV_{biomass\ feedstock}}} \quad (4)$$

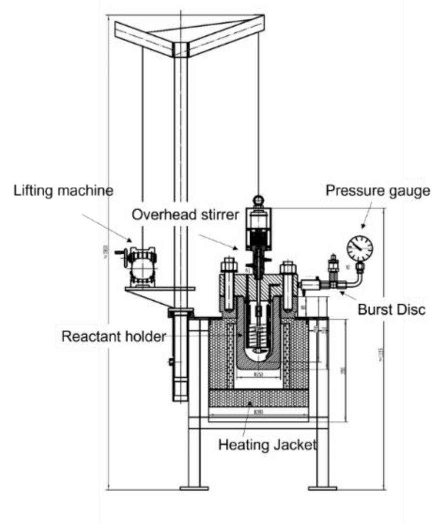

Figure 1. Hydrothermal reactor.

3. Results and discussions

3.1. The effect of process parameters on hydrochar yield

The effect of two parameters, which are the substitution percentage of co-feedstock (LDPE in this work), and reaction temperatures, on the hydrochar yield through hydrothermal carbonization (HTC) was investigated. The hydrothermal carbonization (HTC) process involved subjecting a mixture of water hyacinth (WH) and low-density polyethylene (LDPE) to a temperature of 230 °C with varying LDPE substitution amounts. The results are presented in figure 2. As observed, the introduction of LDPE enhanced the yield of hydrochar, but this effect was notable up to a substitution amount of 10 g (12.5% substitution percentage). This enhancement can be attributed to the synergistic interaction between WH and LDPE. In the investigated HTC conditions, the majority of smaller LDPE molecules dissolved in the aqueous phase, resulting in the generation of active compounds. These compounds played a role in producing larger intermediate building blocks, such as aromatic compounds and low molecular weight substances functionalized with oxygen. This occurred through various processes like condensation, cyclization, and cross-linking reactions. These intermediate building blocks then played a pivotal role in constructing a more condensed carbon structure through processes of polymerization and aromatization reactions, ultimately resulting in the formation of hydrochar. Similar result was reported by Zhang et al.[17]. Moreover, the high carbon content in the LDPE could also enhance the production of high condensable char, the hydrochar, by acting as a catalyst during the HTC process [18]. On the other hand, further increasing of LDPE amount could inhibit the hydrochar yield. This might because as the amount of LDPE increased, some of the LDPE might form a cover on the WH and subsequently bring antagonistic effect on the hydrochar production.

Regarding the reaction temperature, it was noted that an increase in temperature led to a reduction in the yield of hydrochar (refer figure 3). This phenomenon could be attributed to the intensified dehydration and decarboxylation of cellulose and hemicellulose present in the water hyacinth (WH). Consequently, a portion of the macromolecular polymer in the LDPE was directly degraded and eventually promoting the gas formation. Simultaneously, the remaining portion was hydrolyzed, forming compounds, such as furfural, 5-hydroxymethylfurfural, aldehydes, organic acids, alcohols, *etc.*, in the aqueous phase product of HTC [19]. Hence, it can be concluded that the highest hydrochar yield of 29.23 wt% was obtained with 12.5% LDPE substitution percentage, at 200 °C after a holding time of 90 min.

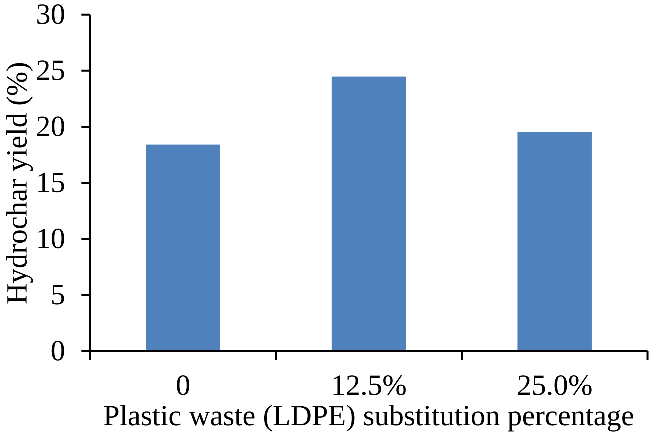

Figure 2. Hydrochar yield at different LDPE substitution percentage via hydrothermal carbonization at 230 °C after 90 min holding time.

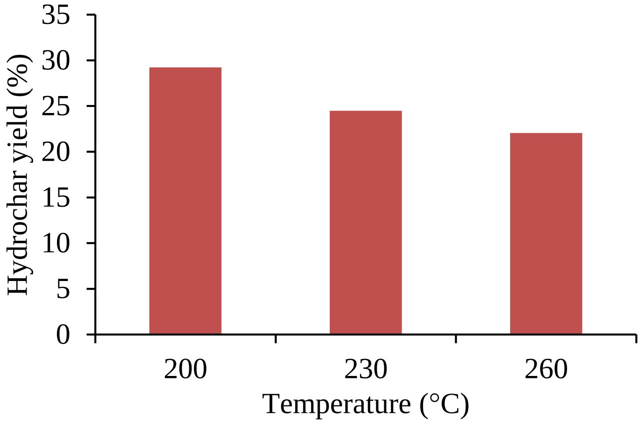

Figure 3. Hydrochar yield at different reaction temperature via hydrothermal carbonization of water hyacinth with 12.5% LDPE substitution rate after 90 min holding time.

3.3. Characterization of biomass and hydrochar

The elemental composition of a biomass feedstock, in this case, water hyacinth and low-density polyethylene (LDPE), was analyzed. This composition reveals the percentage of key elements in these materials, such as carbon, hydrogen, oxygen, and nitrogen. Understanding the elemental composition is essential because it directly influences the energy content of the feedstock. The HHV, expressed in units of energy (MJ/kg), represents the potential energy content of a given material. In this context, it reflects how much energy can be extracted from the biomass through combustion or other conversion processes. Table 1 includes the calculated high heating values (HHV) for both the primary and co-feedstocks. In addition to this, the hydrochar produced via hydrothermal carbonization (HTC) in this study was also characterized for its elemental composition. The HHV values for the hydrochar obtained under various operating conditions were calculated and are reported in table 2 and table 3. As shown, initially, the HHV was 15.54 MJ/kg for water hyacinth alone, and this increased to 17.71 MJ/kg for the hydrochar produced via HTC. Notably, the HHV increased significantly (up to 23.64 MJ/kg) when LDPE was introduced as a co-feedstock. This is due to LDPE's high carbon content, which is an energy-rich element. The impact of reaction temperature on HHV is an important observation. The results (refer table 3) indicate that as the reaction temperature increased, the HHV of the resulting hydrochar also increased. This relationship suggests that higher temperatures in the hydrothermal carbonization process lead to a more energy-dense product. In summary, it can be concluded that the quality of the hydrochar can be enhanced by increasing the energy input into the biomass via the HTC process. The energy density of the resulting char increased with greater reaction severity.

Table 1. Characteristics of biomass feedstock.

Biomass feedstock	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen (%)	Sulphur (%)	High heating value, HHV (MJ/kg)
Low density polyethylene (LDPE)	79.4	14.3	0	6.3	0	50.80
Water hyacinth (WH)	38.1	5.5	1.2	54.4	0.8	15.54

Table 2. Characteristics of hydrochar at different LDPE substitution percentage.

LDPE substitution percentage (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen (%)	Sulphur (%)	High heating value, HHV (MJ/kg)	Hydrochar yield (%)	Energy recovery efficiency (%)
0	50	5.3	0.8	43.8	0.1	17.71	18.42	21.00
12.5	52.5	7.4	0.8	39.3	0	21.03	24.48	25.80
25	56.7	8.1	0.6	34.6	0	23.64	19.52	18.94

Table 3. Characteristics of hydrochar at different reaction temperature.

Temperature (°C)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen (%)	Sulphur (%)	High heating value, HHV (MJ/kg)	Hydrochar yield (%)	Energy recovery efficiency (%)
200	47.8	5	0.5	46.7	0	18.20	29.23	26.67
230	51.2	5.2	0.6	43	0	21.03	24.48	25.80
260	55.3	4.8	0.8	39.1	0	24.69	22.04	27.28

While the HHV provides valuable information about the energy content of the hydrochar, it's important to consider energy recovery efficiency. Energy recovery efficiency is a fundamental metric in the assessment of processes that transform raw materials, such as biomass, into energy-rich products like hydrochar. It's a measure of how effectively the energy within the raw material is converted into a usable form, which, in this case, is the hydrochar. It combines both the quality (HHV) and quantity (yield) aspects of the final product, providing a comprehensive view of the process's performance. The results in table 3 also show that while higher temperatures enhance the HHV, they also decrease the hydrochar yield, which influences the overall energy recovery efficiency. The data in table 2 reveals that the energy recovery efficiency increases as the LDPE substitution percentage rises from 0% to 12.5%. Specifically, the efficiency increases from 21.00% to 25.80%. This indicates that the addition of LDPE up to 12.5% enhances the overall efficiency of the process, resulting in a better conversion of the feedstock into energy-rich hydrochar. However, further increases in the LDPE substitution percentage could inhibit the energy recovery efficiency. Hence, this work suggested that the addition of LDPE in the 12.5% range leads to the most efficient energy recovery.

On the other hand, based on table 3, the result shows that the efficiency is slightly lower at 230°C (25.80%) compared to 200°C (26.67%) and 260°C (27.28%). This indicates that the best energy recovery efficiency is achieved at 260°C. The results imply that the ideal conditions for optimizing energy recovery efficiency in the hydrothermal carbonization process involve a LDPE substitution percentage of approximately 12.5% and a temperature of around 260°C. It's important to note that these results are specific to the experimental conditions and the materials used. The optimum conditions can vary based on the type of biomass, the composition of the co-feedstock, and the specific goals of the process. The findings underscore the significance of carefully selecting LDPE substitution percentages and temperature settings to maximize the energy recovery efficiency in the production of hydrochar.

4. Conclusions

In conclusion, this study explored the influence of two key factors, LDPE substitution percentage and reaction temperature, on hydrochar production through hydrothermal carbonization (HTC). Key findings indicate that LDPE up to a 12.5% substitution enhances hydrochar yield, while higher temperatures boost energy content but reduce yield. The highest yield of 29.23 % occurred with a 12.5% LDPE substitution at 200°C. LDPE also increased energy content, in term of high heating value (HHV). The relationship between reaction temperature and HHV indicated that HHV rose with higher temperatures during the hydrothermal carbonization process. This suggests that elevated temperatures are conducive to the production of more energy-dense hydrochar. On the other hand, the energy recovery efficiency improved with up to 12.5% LDPE but was slightly lower at 230°C. Optimal conditions for energy recovery efficiency were around 12.5% LDPE and 260°C. These findings provide insights into optimizing hydrochar production for sustainable bioenergy.

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