CONVERSION OF ALGAL BIOMASS VIA PYROLYSIS PROCESS INTO PYRO-CHAR PRODUCTION AT WASTEWATER TREATMENT NRC BAIJI

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ABSTRACT

Herein, the algal biomass (AB) was crushed for converted into sustainable, renewable as alternative fuel (pyro-char) by pyrolysis processes during effect of reaction temperatures and contact times. The pyrolysis processes accord by drying AB at 105°C for 24 h to ensure the dried status. In this experiment the range of temperatures by 5g of OS-AB, 5 L h^{-1} flow rate of N_2 pressure, with a fixed residence time of 60 min, and a range of temperatures of 300, 500, and 700°C, were called (AB@60min-300°C, AB@60min-500°C, and AB@60min-700°C) respectively. Optimum pyro-char was produced at 60min, 500°C. At the range of duration times with fixed temperature at 500°C optimum temperature was found in the previous run, and the range of the residence time of 30, 60, and 90 min, were called (AB@500°C-30min, AB@500°C-60min, and AB@500°C-90min) respectively. Optimal pyro-char created at 500°C for 90 min. The energy characteristics of AB and pyro-chars comprised high heating value (HHV), proximal and ultimate analysis, energy recovery (ER), energy yield (EY), atomic ratio, and fuel ratio (FR). The findings revealed that AB had the highest carbon content and HHV. Despite the presence of contaminating components, AB pyrolysis might provide pyro-char (solid carbon fuel) for electricity generation at NRC Baiji.

Keywords: pyrolysis, algal biomass, higher heating value, energy recovery, energy yield.

INTRODUCTION

In this planet, all oil and chemical industries are burdened of dialled with the quantities generated annually during waste water treatment [1]. Biomass, as a renewable energy source, has garnered increasing attention due to concerns about fossil fuel depletion and environmental impacts. Algae offer several advantages as a feedstock for bioenergy production, including rapid growth rates, high lipid content, and the ability to thrive in wastewater. The conversion of algal biomass into valuable products such as bio-oil, syngas, and bio-char through thermochemical processes like pyrolysis is a promising avenue [2]. The NRC Baiji wastewater treatment plant represents a unique and relevant source of algal biomass for this research. Investigating the pyrolysis of this specific biomass will provide insights into its potential for pyro-char production and contribute to the development of sustainable waste-to-energy strategies in the region [3]. Pyrolysis is a thermochemical process that involves the decomposition of organic materials, such as biomass, at elevated temperatures in the absence of oxygen. Unlike combustion, which fully oxidizes the material, pyrolysis breaks down complex organic molecules into simpler compounds, producing a solid (bio-char), a liquid (bio-oil or pyrolysis oil), and a non-condensable gas (syngas) [4].

Absence of oxygen, this is the defining characteristic of pyrolysis. Without oxygen, the biomass doesn't burn. Instead, the heat causes the chemical bonds within the biomass to break down, leading to thermal decomposition [5]. Heat Application: Biomass is heated to specific temperatures, typically ranging from 300°C to over 900°C, depending on the desired products [6]. Decomposition of biopolymers: Biomass is primarily composed of cellulose, hemicellulose, and lignin. During pyrolysis, these complex biopolymers deconstruct into smaller molecules. Products of pyrolysis generally yields three main products. Bio-char (Solid) this is a carbon-rich solid residue, analogous to charcoal. Its properties (surface area, porosity, carbon content) are highly dependent on the pyrolysis conditions (temperature, residence time) [7]. Bio-char has various applications, including soil amendment, activated carbon production, and catalyst support. Bio-oil/pyrolysis oil (liquid), this is a dark, viscous liquid composed of a complex mixture of organic compounds. Its composition can vary significantly based on the biomass feedstock and pyrolysis parameters. Bio-oil has potential as a renewable fuel or as a source of valuable chemicals, though it often requires upgrading due to its high oxygen content and corrosiveness [8]. The key operating parameters that influence pyrolysis like temperature, higher temperatures generally favour gas and bio-oil production, while lower temperatures increase bio-char yield. Heating rate, rapid heating rates favour bio-oil, while slow heating rates favour pyro-char. duration time, short residence times are crucial for fast pyrolysis to minimize secondary reactions and maximize liquid yields. Longer residence times allow for more complete char formation [9].

Biomass particle size, smaller particle sizes allow for more efficient heat transfer and faster decomposition, which can be important for fast pyrolysis. Feedstock Composition the chemical makeup of the biomass (e.g., lignin, cellulose, hemicellulose, protein, lipid content) significantly influences the product distribution and their characteristics. For example, algal biomass with high lipid content might yield different bio-oil compositions compared to lignocellulosic biomass. Presence of catalysts, catalysts can be used to enhance specific product yields, improve product quality, or lower reaction temperatures. In summary, biomass pyrolysis is a versatile thermochemical conversion technology that transforms organic matter into valuable solid, liquid, and gaseous products by carefully controlling reaction conditions in the absence of oxygen. The choice of pyrolysis method depends on the desired end products and their specific applications.

Pyro-char, a solid carbonaceous substance, has a variety of applications, including soil amendment, activated carbon synthesis, and catalytic support. The exploitation of algal biomass from wastewater treatment provides a sustainable waste management solution while also providing a value-added product. This study focuses on the pyrolysis of algal biomass from the NRC wastewater treatment plant in Baiji, Iraq, to produce pyro-char. This research aims to characterize the pyro-char produced and evaluate the efficiency of the pyrolysis process for converting algal biomass from this source into a useful product. To prepare and describe AB, establish its suitability under of pyrolysis process, and then create (pyro-char) solid carbon fuel underneath discovered to be better than reaction temperatures and contact times, as well as rid the environment of oils polluting pollutants.

EXPERIMENTAL

Preparation of algal biomass

The raw material (AB) for this investigation was obtained from wastewater treatment units operated by North Refineries Company (NRC) in Baiji, Iraq. The experiment was carried out on a (AB) sample, which was washed manually, exposed to sunlight for a day, and then dried at 105°C for 24 h [10]. It was then physically crushed and kept as powder to achieve a homogeneous and compact size.

Pyrolysis processes of algal biomass

In this experiment, algal biomass, crushed well and then called (AB). Fig. 1 shows the pyrolysis processes of AB for pyro-char production. On one hand, pyro-char at a range of temperatures was produced of 5g AB feed amount, 4 L min^{-1} of N_2 pressure flow rate, with a constant residence time of 60 min, and a range of temperatures of 300, 500, and 700°C, were labelled (AB@60min-300°C, AB@60min-500°C, and AB@60min-700°C) respectively. In this run, the best temperature was 500°C, and the highest high heating value [HHV] reached 7.91 MJ kg^{-1}, as shown in Table 1. On the other hand, pyro-char was formed using a range of contact periods, 5g of AB, 4 L min^{-1} of N_2 pressure flow rate, and a fixed temperature of 500°C (the optimal temperature was discovered in the previous test). As a result, the residence time ranges of 30, 60, and 90 min were designated (AB@500°C - 30min, AB@500°C - 60min, and AB@500°C - 90min) respectively. Furthermore, Table 1 shows that the best duration time for this run was 90 min, and the maximum HHV was 9.95 kJ kg^{-1}. Pyrolysis was conducted in a 100 mL Alumina Ceramic Crucible Boat Sample Holder with No Hole, 80×12×10mm, using a N_2 gas flow rate. The horizontal furnace flow rate was 15°C min^{-1}. The horizontal furnace was automatically cooled to room temperature one at a time. Pyro-char samples were oven-dried at 105°C for 24 h before being pulverized into fine powders for further examination. All experiments were done a minimum of three times.

Calculations

The raw material (AB) prepared, and pyro-char produced were evaluated as described in the following sections. The HHV was calculated using a bomb calorimeter in accordance with (ASTM E711) [12]. The weight and weight percentage of pyro-char yield were determined by dividing the pyro-char yield by the AB feed amount [11 - 13]. The upgrading of AB qualities as pyro-char by energy attributes was addressed in Eqs. (1 - 6) [14]. The CHN-O (elemental percent) was calculated using element combustion. The volatile matter was tested using ASTM E872-82 [15]. The ash content was tested in an electric muffle furnace, and the ash percentage was calculated using the ASTM D1102-84 standard technique for ash [16]. The estimated value of fixed carbon was derived by summing ash and volatile matter and subtracting 100 %. The energy characteristics of AB as a pyro-char were detailed. Eq. (1) was applied sequentially to analyse the pyrolysis process [16]:

$$\text{Pyro-char yield (\%)} = \frac{\text{pyro} - \text{char weight}}{\text{AB weight}} \times 100 \quad (1)$$

The oxygen content (O %) determined from the ultimate analysis data by Eq. (2):

$$\text{Oxygen \% (O)} = 100 - \text{carbon \% (C)} - \text{hydrogen \% (H)} - \text{nitrogen \% (N)} \quad (2)$$

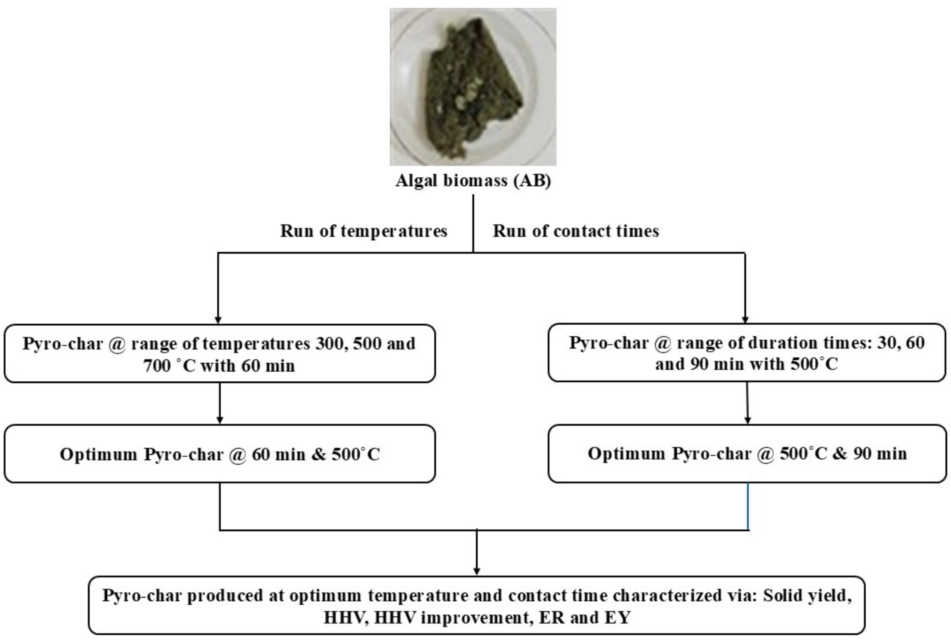

Fig. 1. Schematic diagram of pyrolysis processes of AB into pyro-char production.

Eq. (3) is used to compute the fixed carbon (FC %) from the proximate analysis:

Fixed carbon (FC) % = 100 - Ash % - volatile matter (VM) % (3)

The fuel ratio, a combustibility index, is calculated by Eq. (4):

$$\text{Fuel ratio} = \frac{FC}{VM} \quad (4)$$

Eq. (5) can be used to determine the ER %:

$$\text{Energy recovery (ER)} = \frac{\text{HHV of pyro-char}}{\text{HHV of AB}} \times 100 \quad (5)$$

The EY % can be determined finally by Eq. (6) as follows:

$$\text{Energy yield (EY)} = \text{pyro-char yield} \times \text{ER} \quad (6)$$

RESULTS AND DISCUSSION

Pyro-char yield of algal biomass

The pyro-char yields were calculated according to the Eq. (1). The pyrolysis processes of AB by a different range of temperatures, and various contact times, and enhanced the pyro-char produces via HHV, HHV improvement, fuel energy recovery (ER), and energy yield (EY) were investigated. Table 1 and Fig. 2 show the solid produced of pyro-char at (a) range of temperatures, and (b) range of contact times, respectively. The results showed that the solid yield was increased from 300°C to 500°C about 11.4 % then decreased to 16 % at 700°C which mean the best temperature is 500°C in the run of temperature [17]. While in the range of contact times the highest solid yield was at 90 min reached 86.8 % compared to 30 min which was 83.6 % this finding

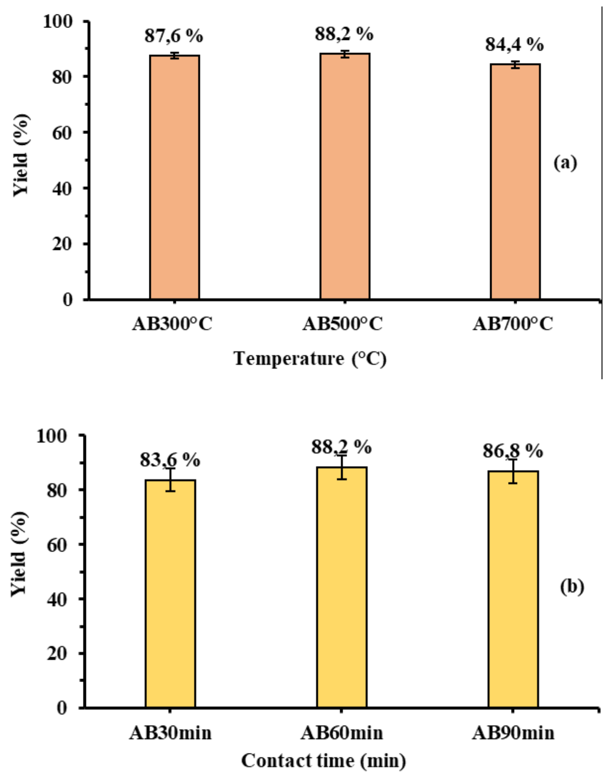

Fig. 2. Pyro-char yield of AB via pyrolysis processes, (a) pyro-char produced at range of temperatures, (b) pyro-char produced at range of contact times.

Table 1. Solid yield mass and percentage products, HHV, HHH improvement, ER, and EY.

Parameters	Values	Yield, g	Yield, %	HHV, MJ kg^{-1}	HHV improvement	ER, %	EY, %
Raw material	AB			17.22			
Range of temperatures	300°C	4.38	87.6	27.12	26.12	57.49	137.96
	500°C	4.41	88.2	27.95	26.95	62.31	143.15
	700°C	4.22	84.4	27.42	26.42	59.23	134.39
Range of contact times	30 min	4.18	83.6	26.35	25.35	53.01	127.92
	60 min	4.41	88.2	27.95	26.95	62.31	143.15
	90 min	4.34	86.8	27.15	26.15	57.66	136.85

lead to best temperature is 500°C with 90 min at these conditions best reactions accorded like; decarboxylation and dehydration processes, agreed with [18].

High heating value profile

The HHV of pyro-char produced at range temperatures and contact times as shown in Table 1, Fig. 3. Fig. 3a HHV of AB and pyro-chars produced at various temperatures, while Fig. 3b HHV of AB and pyro-chars produced at range of contact times. On one hand the results showed the HHV values were improved about 159.23 % from 17.22 AB to 27.42 of pyro-char produced at 500°C at the temperature run based on [19]. On other hand at the range of contact time the HHV was decrease at highest contact time at 90 min this finding lead to best temperature was 500°C and 60 min. The reactions decarboxylation and de hydration were affected of the pyro-char produced which enhanced of the HHV values, agreed with [20].

High heating value improvements

The HHV of pyro-char produced at various temperatures and residence times is shown in Table 1, Fig. 4. Fig. 4a HHV improvement of pyro-chars produced at various temperatures, while Fig. 4b HHV improvement of pyro-chars produced at different contact residence times. At range of temperature the HHV improvement were 26.12 at 300°C, 26.95 at 500°C, and 26.45 at 700°C, we can see the best HHV improvement accorded at 500°C this finding was agreed with HHV enhanced at same temperature, agreed with [21].

Energy recovery

The ER is calculated after pyro-char is produced to determine the ER, the Table 1, and Fig. 5 shows the ER of pyro-char produced by a range of temperatures and different duration times. Fig. 5a ER of pyro-char produced during the range of temperatures, and Fig. 5b ER of pyro-char produced at various contact times. The percentage of ER at all cases were up to 50 % energy recovered while highest ER was done at 500°C, and 60 min best conditions were achieved. Which in turn allowed decarboxylation and dehydration reactions to occur freely, agreed [22].

Energy yield

The ER of pyro-char produced during pyrolysis of

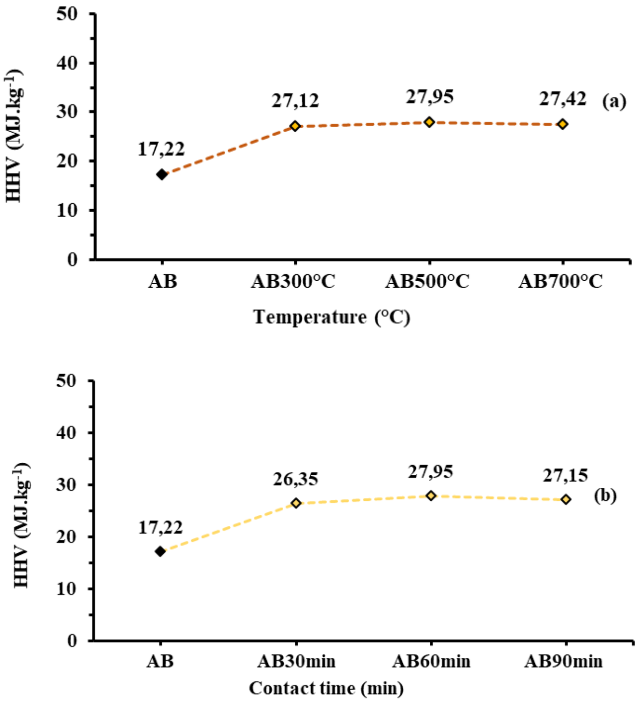

Fig. 3. HHV of AB and pyro-char, (a) pyro-char produced at range of temperatures, (b) pyro-char produced at range of contact times.

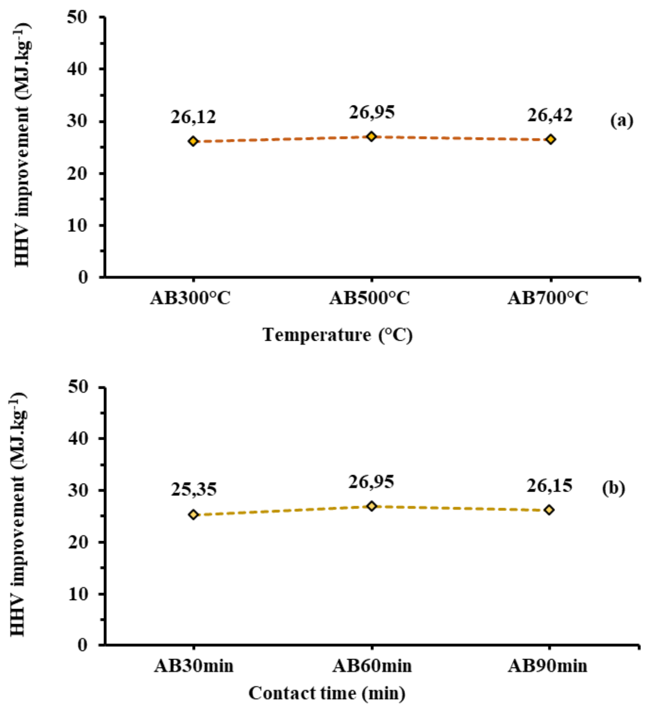

Fig. 4. HHV improvement of pyro-char, (a) pyro-char produced at range of temperatures, (b) pyro-char produced at range of contact times.

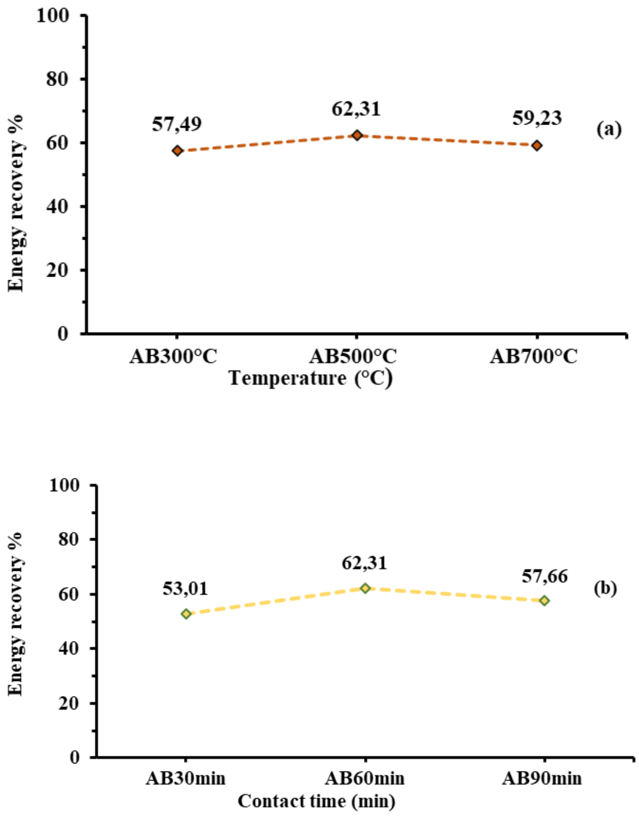

Fig. 5. ER of pyro-char, (a) pyro-char produced at range of temperatures, (b) pyro-char produced at range of contact times.

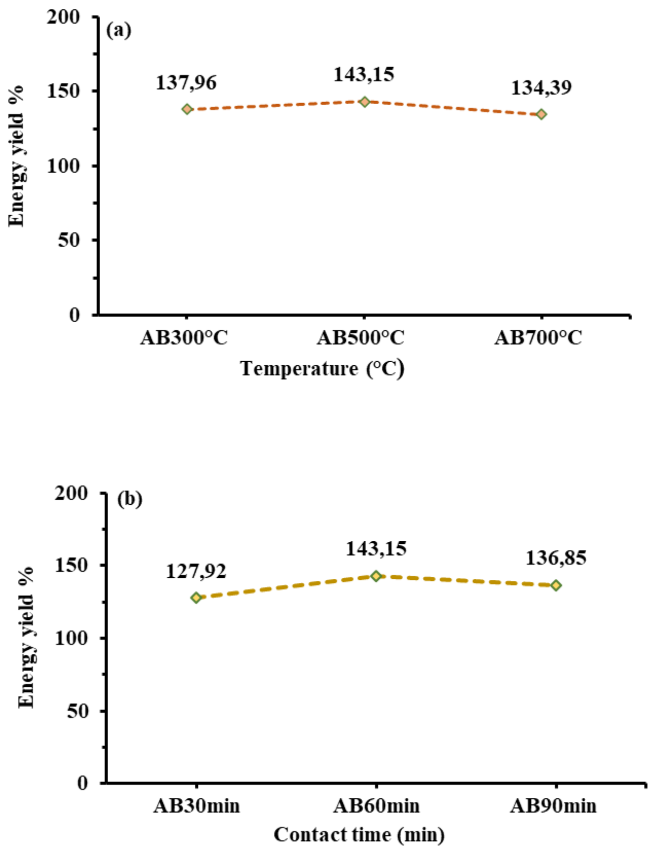

Fig. 6. EY of pyro-char, (a) pyro-char produced at range of temperatures, (b) pyro-char produced at range of contact times.

AB as shown in Table 1, and Fig. 6. Fig. 6a EY of pyro-char produced at different temperatures, and Fig. 6b EY of pyro-char produced at various contact times. As a result, among the EY highest one was 143.15 at 500°C, and 60 min, while lowest on was 134.39 at 700°C, and 60 min this finding showed 500°C, and 60 min was suitable for conversion of AB during pyrolysis process during these conditions agreed with [23].

Life cycle analysis

Fig. 7 shown the life cycle analysis (LCA) A theoretical LCA is applied to assess the pyrolysis conversion of AB into pyro-char. The assessment aims to quantify potential benefits and drawbacks, including energy efficiency, carbon emissions, and resource utilization. As shown in the Fig. 7, the HHV exhibits a consistent upward trend with increasing reaction temperature and contact time, rising from 71.22 MJ kg^{-1}in the raw AB to a pyro-char of 27.95 MJ kg^{-1} at 500°C and 60 min [24]. This reflects the enhanced energy content achieved through effective dehydration and decarboxylation processes. Similarly, the HHV improvement, ER, and EY increases from 300°C to 500°C at ranges of temperatures, while there was no effect of the contact time, it was found that the best contact time is 60 min, indicating improved combustion properties due to greater energy properties. Conversely, mass loss also increases with treatment severity, reaching up to 16.4 %, highlighting the thermal decomposition and release of light compounds. The overall pattern confirms that higher reaction temperature and longer contact times significantly improve the fuel quality of AB, though with increased material loss an important trade-off for optimizing conversion efficiency agreed with [25 - 29].

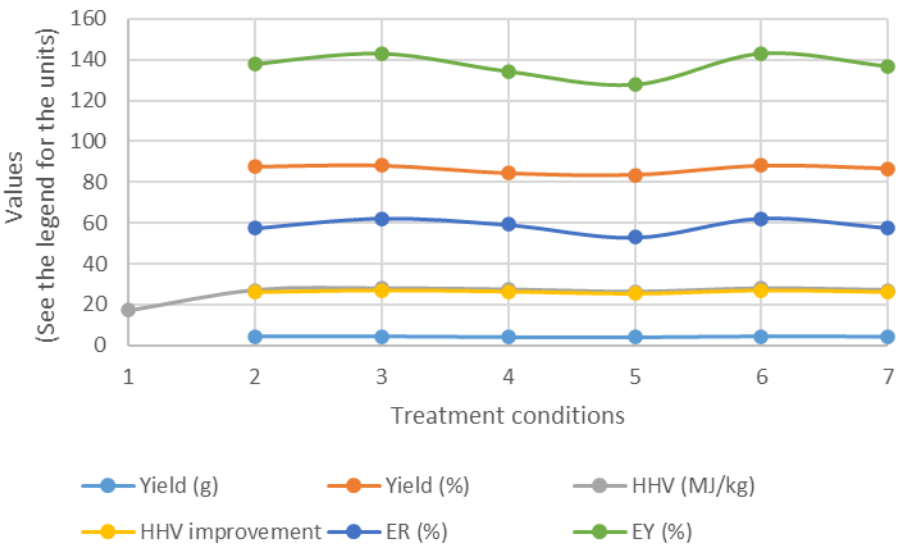

Fig. 7. The effects of pyrolysis treatment conditions on the solid yield, HHV, HHV improvement, ER, and EY.

CONCLUSIONS

The pyro-char produced and energy evaluation by pyrolysis process of AB were detailed in this work. The results proved the effect of temperature on the pyro-char yield up to 500°C, then decreased. While the effect of the contact time on the pyro-char yield was a positive effect, it was shown that the solid yield increased with the increase in the contact time till 60min then decreased, which indicates that the effectiveness of the impact of the contact time in this process. For the future work best, conditions were 500°C, and 60 min. The contact time of 60min was found to be the most suitable for achieving efficient conversion. During the pyrolysis process, several thermochemical reactions occurred, as indicated by changes in fuel properties and the release of gaseous byproducts such as CH_4, CO_2 and CO. These gases contribute to improving the combustion characteristics of the produced pyro-char.

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Authors' contributions

N.Kh.: conceptualized the study and supervised the research process; M.G.: conducted the data curation, performed the formal analysis, and contributed to the original draft preparation; Q.A.: was responsible for software development, data visualization, and validation of results; G.B.: carried out the investigation, managed resources, and contributed to project administration; O.G.: performed the experimental work and assisted in reviewing and editing the manuscript; M.A.: contributed to the methodology design, supported funding acquisition, and participated in the writing of the original draft; O.H.: conducted the literature review, interpreted the results, and participated in the manuscript revision and editing.

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