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Co-pyrolysis for bio-oil production via fixed bed reactor using date seeds and plastic waste as biomass

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A R T I C L E I N F O

Keywords:
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A B S T R A C T

The consumption of plastic bottles is relatively high in the United Arab Emirates (UAE). Therefore, in this study authors investigated the potential of combined plastic waste and locally available biomass (date seeds) to produce value-added products (bio-oil, bio-char and syngas) via pyrolysis process. The experiments were performed in a fixed bed pyrolizer, operated at different temperatures. Experimental results showed that 500 °C would be a better option for a higher bio-oil yield (59.16%), while lower temperatures (300 °C) produced more bio-char yields (24.97%). A plastic ratio of 70% gives the highest bio-oil content (62.57%), and lowest amounts of bio-char (12.14%). Experiment performed at 400 °C with a plastic waste ratio of 30% have the highest bio-oil density (1.020 g/cm^3). The results obtained in this study showed that the co-pyrolysis of plastic waste and date seeds are suitable for bio-oil production as sustainable biofuel in UAE.

1. Introduction

The intensive utilization of fossil fuels has several negative environmental impacts, such as greenhouse gas emissions, global warming, and climate change. Therefore, great attention has been paid to alternative sources of energy, including lignocellulosic biomass to produce bioenergy and biofuels [1,2]. Lignocellulosic feedstocks can be transformed into value-added products through chemical, biochemical, or thermochemical paths [3]. Chemical processes utilize chemicals and catalysts to produce for example biodiesel by means of transesterification and esterification reactions. Biochemical processes use living microorganisms (such as bacteria) to break down the biomass and transform it into biodegradable products, usually by means of anaerobic digestion and fermentation [4]. Thermal methods use heat or thermal energy and include processes such as drying, torrefaction, combustion, gasification, and pyrolysis [5–7]. From all these processes, great attention has been paid to pyrolysis since it is a cost-effective and environmentally friendly technology [8]. Biomass pyrolysis is a thermochemical process that can be used to produce bio-oil, bio-char, and syngas in the absence of oxygen [9]. Pyrolysis processes can be categorized in slow, fast, and ultrafast. Slow pyrolysis (also well-known as conventional pyrolysis or carbonization) utilizes temperatures between 300 and 500 °C, low heating rates

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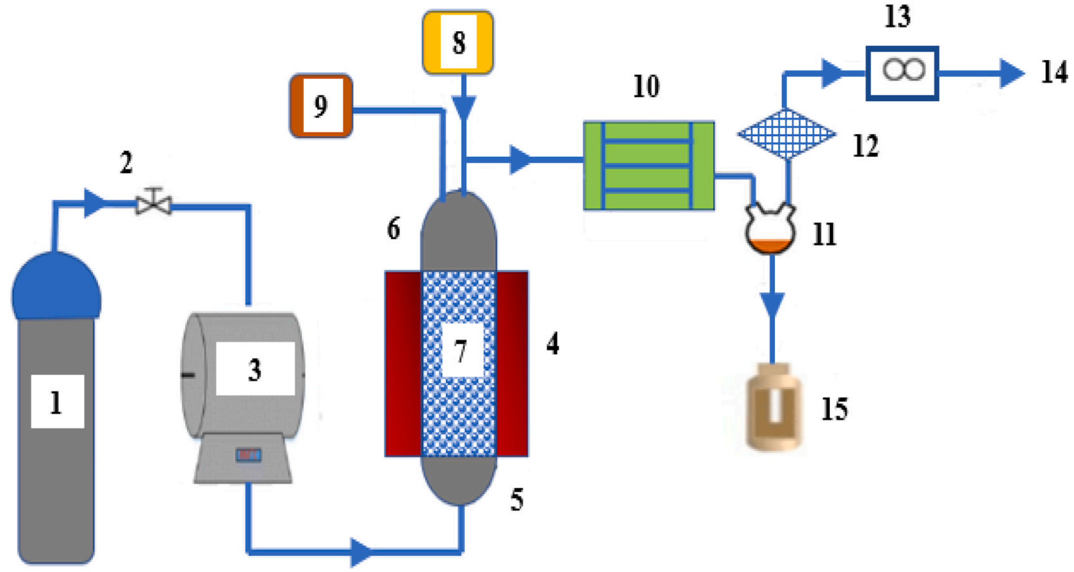

Fig. 1. Set up of the pyrolysis reactor used in the experimental work (1) nitrogen gas tank, (2) flow controller, (3) gas heater, (4) furnace with electrical tubes, (5) char collector, (6) pyrolysis reactor, (7) biomass bed, (8) biomass lock hopper, (9) Thermocouple (10) condenser, (11) condensation & gaseous separator, (12) filter, (13) gas flow meter, (14) gas output (15) extracted bio-oil.

(0.1–1 °C/min), high residence times (up to 2 h), and relatively large particle size (between 5 and 50 mm) to convert biomass into bio-char. The bio-char obtained from slow pyrolysis has a high solid production of about 45%. Fast pyrolysis is utilized to convert the biomass into a liquid product called bio-oil. This process usually occurs at higher temperatures 450–700 °C, higher heating rates (1–200 °C/s), very short retention times (about 20 s), and uses particle size inferior to 1 mm. The bio-oil obtained from the fast pyrolysis represents about 75% of the total products obtained in this process. Ultrafast pyrolysis utilizes temperatures superior to 800 °C, very short retention times (1 s), very high heating rates (above 1000 °C/s), and small particle size (inferior 0.2 mm) to generate non-condensable syngas (hydrogen, carbon dioxide, carbon monoxide, methane, ethylene, and ethane) [10–13]. Hai et al. [14] investigated the potential of date palm waste for bio-oil production. The authors concluded that the bio-oil obtained has a relatively high viscosity and heating value and that it can be further refined and utilized in biofuel applications. Similar findings were obtained by Bharath et al. [15]. Furthermore, Raza et al. [16] simulated the pyrolysis process of combined date seeds and coffee waste for bio-oil production. The results obtained in their study show that by optimizing the simulation process it is possible to obtain high amounts of bio-oil. Although the co-pyrolysis of date palm seeds and waste products has already been investigated, the authors could not find research on this combined solution [17]. Other studies involve other types of hybrid technologies and do not specifically focus on the potential and optimization of co-pyrolysis of date seeds and plastic waste. Pyrolysis is a promising technology for the production of value-added products that can be used to decrease the production of energy from fossil fuels. However, research has shown that the bio-oil obtained in this process still has a reduced combustion efficiency when compared with fossil fuels [18]. Also, pyrolysis systems are still very energy intensive processes, costly, complex, and produce high amounts of carbon dioxide [19]. As a result, there is a continuous search for more effective, environmentally friendly, and efficient ways of producing valuable products from pyrolysis processes. Co-pyrolysis has been reported as an effective strategy to produce bio-oil with superior traits (e.g. higher oil yield, lower water content, and higher caloric value) than conventional pyrolysis [18,20]. In this study a co-pyrolysis process for the thermal conversion of plastic waste and date seeds into bio-oil, bio-char, and syngas was designed. The experiments were performed in a fixed bed reactor and the quality and quantity of the produced materials was analyzed, to ensure the suitability of the bio-oil as an alternative fuel to the conventional energy sources. For this, different pyrolysis temperatures (300 °C, 400 °C, and 500 °C) and plastic waste ratios (30%, 50%, and 70%) were used, and their effect on product yields and properties was analyzed.

2. Materials and methods

2.1. Feedstocks

Date seeds were provided by local private households, while the shattered plastic was obtained from the company Plastics Alliance (FZE), both in the Emirate of Sharjah, United Arab Emirates. Prior to griding, the date seeds were washed and dried naturally for 48 h. After that, the samples were dried in the oven to a moisture content of 5% (or less) (model SLN 180 from POL-EKO-APARATURA, Poland) for 5 min and soaked in liquid nitrogen for 1 min. The date seeds were grinded (grinder from Retsch GmbH) to a particle size of 1–2 mm and placed again in the oven at 103 °C for 24 h to remove any extra moisture. The plastic waste was shattered and did not require additional grinding. The proximate analysis was done using the ASTM D121 standard [21] and the ultimate analysis was done using a CE Instruments Flash EA 1112 Series CHNO Analyser, Thermo Quest, Italy.

Table 1
Ultimate and proximate analysis of date seeds and plastic waste.

		Date seeds (%)	Plastic waste (%)	Date seeds (%)	Plastic waste (%)
Proximate Analysis	Moisture	4.9	–	4.5–4.9	0.0–2.4
	Volatile Matter	77	63	62–84	51–99
	Fixed Carbon	7.7	7.7	6.9–9.1	0.0–2.4
	Ash	7.7	25	2.4–12	0.0–7.6
Ultimate Analysis	C	45	42	40–48	39–90
	H	5.6	6.5	7.2–9.7	3.1–14
	O	47	25	37–53	1.7–18
	N	1	0.78	0.16–3.2	0.02–0.43
	S	0.8	0.06	–	0.0–1.8
Source		Current study	Current study	[22,23]	[24–27]

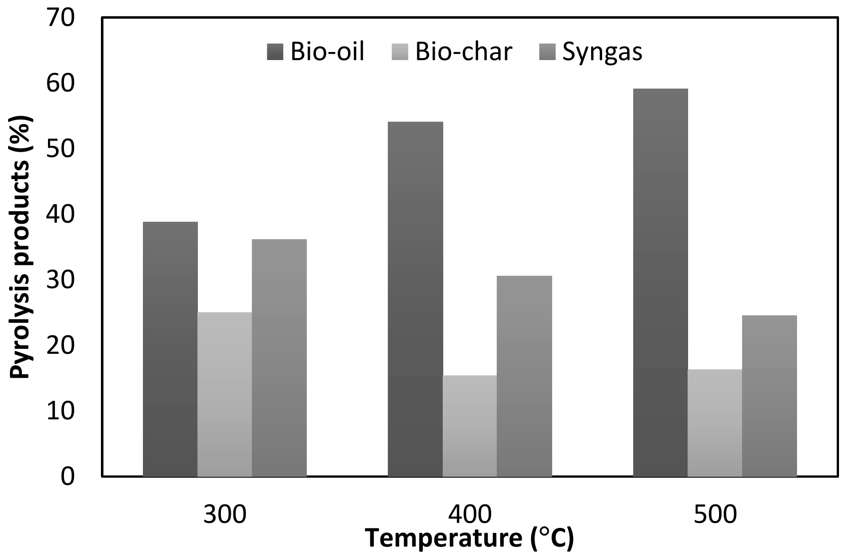

Fig. 2. Effect of different temperatures on the pyrolysis products.

2.2. Experimental procedure

A fixed bed pyrolysis reactor (Model number BFK-1L/12.5 from Weihai Borui Chemical Machinery Mfg Co., Ltd., China) was used for the co-pyrolysis of date seeds and plastic waste. In the pyrolysis experiments, 100 g of date seeds biomass was added into the 1 L stainless-steel reactor at different ratios with plastic waste (50%, 60%, and 70%) and pyrolyzed at different temperatures (300 °C, 400 °C, and 500 °C), under the following operational parameters: heating rate of 50 °C/min, nitrogen gas flow rate of 100 mL/min, working pressure 12.5 MPa, impeller stirring speed up to 1200 RPM, and impeller motor power of 80 W. Fig. 1 shows the set up utilized in the experiments. After adding the biomass into the vessel, the reactor was closed and purged with nitrogen for 2 min at a flow rate of 100 mL/min to ensure anaerobic conditions. The samples were heated from room temperature up to required temperature at a heating rate of 10 °C/min.

2.3. Statistical analysis

The software GraphPad Prism version 9.1.2. was utilized to investigate statistically significant differences between the results ($p < 0.05$). For this, the Shapiro-Wilk normality test was applied to analyze if results are modeled by a normal distribution. This test considered the null hypothesis that the population is normally distributed. As the results obtained were not normally distributed, the non-parametric Friedman test (one-way repeated measure data) was used to investigate the differences between the results. This test was followed by the post hoc dunn's multiple comparisons test, which was used to compare the mean rank of each column with the mean rank of every other column and to investigate statistically significant differences between the results ($p < 0.05$).

3. Results and discussion

3.1. Parametric study

Table 1 illustrates the ultimate and proximate analysis of date seeds and plastic waste utilized in the experiments.

As it can be seen from Table 1, the moisture content of the data seeds was approximately 5%, and the volatile matter contents for both feedstocks varied between 63 and 77%. The percentage of fixed carbon was 7.7% for both substrates. The amount of ash was 7.7%

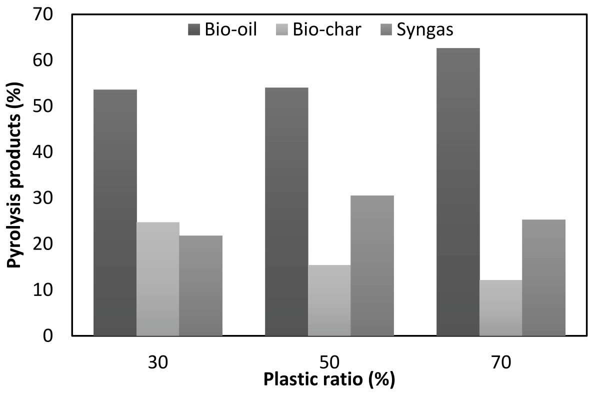

Fig. 3. Effect of different plastic ratios on pyrolysis products.

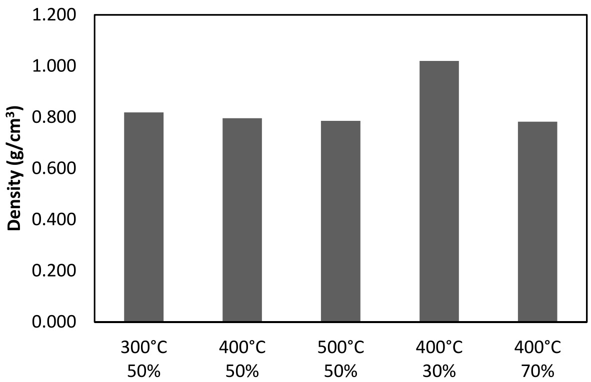

Fig. 4. Effect of different pyrolysis temperatures and plastic waste ratio in the bio-oil density.

for data seeds and 25% for plastic waste. The ultimate analysis revealed relatively high percentages of carbon and oxygen, and relatively low percentages of hydrogen, nitrogen, and sulphur. The results obtained in this study are comparable with the values reported in literature [23,24,26].

Fig. 2 illustrates the effect of pyrolysis temperature on the products yields, utilizing a constant plastic ratio of 50%. The highest percentage of bio-oil (59.16%) was obtained at 500 °C, while the lowest amount of bio-oil, bio-char and syngas were produced at 300 °C, 400 °C, and 500 °C, respectively. As it can be seen from the figure, when the pyrolysis temperature increases, the percentage of bio-oil yield tends to increase, while the percentage of bio-char and syngas tend to decrease. Statistically significant differences were found between the pyrolysis temperatures and the bio-char products yield.

Joardder et al. [28] also studied the utilization of waste date seeds for bio-oil production by means of pyrolysis. The experiments were performed in an externally heated fixed bed reactor with a temperature range between 400 and 600 °C. The authors obtained a maximum liquid output of 50 wt% by performing pyrolysis at 500 °C. Similar conclusions were obtained in a study performed by Irfan et al. [29]. The authors utilized halophyte grass (*Achnatherum splendens* L.) for bio-oil, bio-char, and syngas production. The results obtained showed higher bio-oil yields at 500 °C, and that the bio-chair yields tend to decrease with the increment of the pyrolysis temperature [23,28]. However, the bio-oil yields obtained in current study are higher than the yields obtained by other researchers; the bio-char results are lower than the values reported in the literature.

Fig. 3 shows the effect of different plastic ratios pyrolyzed at the constant temperature of 400 °C for main products. The maximum percentage of bio-oil was obtained at 70% plastic ratio, while the highest amount of bio-char and syngas products were obtained at a plastic ratio of 30%, and 50%, respectively. The lowest amount of biochar was produced at a plastic ratio of 70%, while the lowest amount of syngas was produced at a plastic waste ratio of 30%. Overall, bio-oil yields tend to increase with increments in the plastic ratio, while the amount of bio-char tends to decrease with increments in the plastic ratio. Similar findings were reported in a study performed by Rathnayake et al. [30]. The authors concluded that high ratios of plastic have a positive impact on higher bio-oil yield due to low bio-char production and due to low moisture contents in plastic waste.

3.2. *Bio-oil properties*

The results of the bio-oil density are shown in Fig. 4. As it can be seen, the highest bio-oil density (1.0 g/cm^3) was obtained for samples that were pyrolyzed at 400 °C, with a plastic waste ratio of 30%, and a date seeds ratio of 70%, while the lowest bio-oil density (0.78 g/cm^3) was obtained in samples that were pyrolyzed at 400 °C with a plastic waste ratio of 70%. Statistically significant

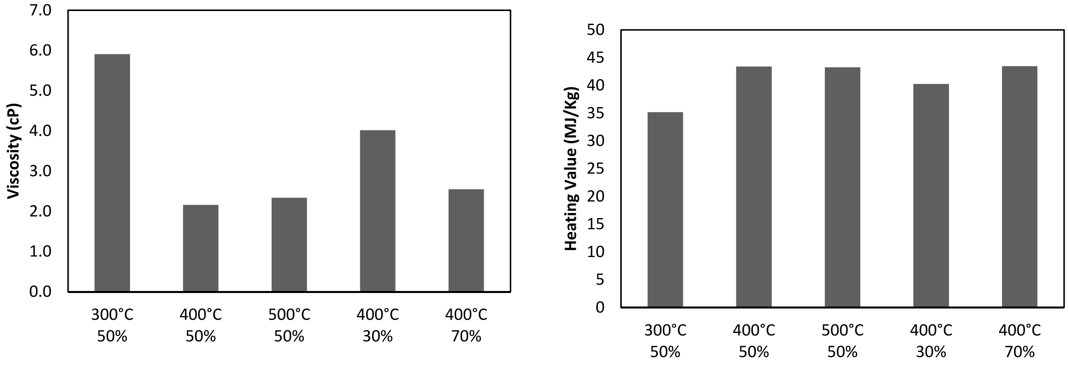

Fig. 5. Effect of different pyrolysis temperatures and plastic waste ratio in the bio-oil (a) viscosity; (b) heating value.

differences were found between the pyrolysis temperatures and the bio-oil density.

Bio-oil with high density is a desirable condition when it comes to the production of biofuels since it influences the energy value of the fuel. High density values tend to increase the energy content of the fuel [31]. By doing co-pyrolysis of date seeds and plastic waste it was possible to obtain a bio-oil with higher density (1.0 g/cm^3) than biodiesel (0.85 g/cm^3). These results show that waste date seeds can be a great candidate for the production of bio-oil.

The effect of different pyrolysis temperatures and plastic waste ratio in the bio-oil viscosity and heating value are shown in Fig. 5a and Fig. 5b, respectively. The highest viscosity (5.9 cP) was obtained for samples that were pyrolyzed at 300 °C with a plastic waste ratio of 50%, followed by samples that were pyrolyzed at 400 °C with a plastic waste ratio of 30% (4.0 cP), at 400 °C with a plastic waste ratio of 70% (2.6 cP), 500 °C with a plastic waste ratio of 50% (2.3 cP), and at 400 °C with a plastic waste ratio of 50% (2.2 cP). Overall, lower pyrolysis temperatures and plastic waste ratio tend to increase the viscosity of the bio-oil. When it comes to the heating value, samples with a plastic waste ratio of 70% that were pyrolyzed at 400 °C had the highest heating value (43.47 MJ/kg), followed by samples with a plastic ratio of 50% pyrolyzed at 400 °C (43.3 MJ/kg), plastic ratio of 50% pyrolyzed at 500 °C (43.28 MJ/kg), plastic ratio of 30% pyrolyzed at 400 °C (40.27 MJ/kg), and plastic ratio of 50% pyrolyzed at 300 °C (45.19 MJ/kg). Overall, these results show that lower pyrolysis temperatures and plastic waste ratios tend to decrease the bio-oil heating value, while higher pyrolysis temperatures and plastic waste ratio tend to increase the bio-oil heating value.

The heating value of the bio-oil obtained in this study (by co-pyrolysis) was higher than the bio-oil of date seeds reported in literature, which shows the potential of co-pyrolysis of date seeds and plastic waste for bio-oil production [28]. Also, date seeds have a higher heating value than other feedstocks like wastepaper and sugarcane bagasse [28].

4. Conclusion

This study investigated the potential of co-pyrolysis of plastic waste and date seeds for bio-oil, biochar, and syngas production. The results obtained in this study show that at a pyrolysis temperature of 500 °C it was possible to obtain a maximum bio-oil yield of 59.16%, while samples pyrolyzed at lower temperatures (300 °C) produced more bio-char yields (24.97%). High plastic ratios (70%) produced bio-oil yields (62.57%), while low plastic ratios (30%) produced higher amounts of bio-char (24.68%). Overall, the results obtained in this study show that the bio-oil yields increase with the increment of plastic waste ratio and operating pyrolysis temperature. Higher amounts of date seeds and low operating temperatures produce high amounts of bio-char. Increasing the pyrolysis temperature while maintaining a constant feedstock ratio enhanced bio-oil yields. In addition, higher plastic ratios at constant temperature also boosted bio-oil yields. The highest bio-oil yield was reported at 400 °C using 70% plastic waste ratio. The results of the bio-oil properties show that the highest density and viscosity were 1.0 g/cm^3 and 5.9 cP, respectively. Waste date seeds are a great candidate for the production of bio-oil that can be used to decrease the share of fossil fuels in the transportation sector. Future research will involve the development and optimization of bio-based catalysts for the production of high-quality and cost-efficient bio-oil, biochar, and syngas.

Author contribution

All authors contributed to the study conception and design. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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