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CO-PYROLYSIS OF RICE HUSK AND DATE PALM SEEDS: INFLUENCE OF TEMPERATURE AND BLENDING RATIO ON PRODUCT YIELDS AND GAS EVOLUTION

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Article Info

Abstract

In this study, the effects of blending ratio and temperature on product distribution during co-pyrolysis of rice husk (RH) and date palm seed (DS) were investigated. The pyrolysis products were generated using fixed bed reactor and gaseous products were analyzed using gas chromatography. The solid yields consistently decreased over the entire temperature range from 300 to 600 °C for all biomass feedstocks. The liquid yield for 100%RH was found to increase to 35.35% from 300 to 500 °C, with the maximum yield observed at 500 °C. At higher temperatures, the liquid yield decreased. For 100%DS, the liquid yield increased up to 400 °C, reaching a maximum of 48.59% at this temperature, and then decreased at higher temperatures. An increasing proportion of DS led to a decrease in char and gas yield, thereby increasing liquid yield. Among the blends, the maximum liquid yield was obtained with a 75% proportion of DS in the blend. The solid yield exhibited a negative deviation, while the liquid yield showed a positive deviation across most temperatures and blending ratios. Thus, the co-pyrolysis of RH and DS reduced the char yield and promoted the formation of bio- production. CO2 yields from all blends were maximum in the temperature range of 400-500 °C. The 25%DS+75%RH blend exhibited higher CO yield than the 100%DS sample across all temperature ranges. The 50%DS+50%RH and 75%DS+25%RH blends showed higher CO yields than the individual samples during the isothermal stage. All blends produced higher H2 yields than the individual samples at 500-600 °C, with the 25%DS+75%RH and 75%DS+25%RH blends exceeding the individual samples during the isothermal stage. The 25%DS+75%RH and 75%DS+25%RH blends also had higher CH4 yields than individual samples in the 400-500 °C range, and the 75%DS+25%RH blend showed the highest CH4 yield compared to individual samples during the isothermal stage.

Keywords:
Co-pyrolysis; Rice husk; Date palm seed; Products distribution; Synergistic effect; gas evolution

Introduction

The depletion of conventional energy resources and escalating environmental concerns have necessitated a shift towards renewable energy sources. Among these, biomass has emerged as a pivotal player in this transition [1]. As a globally dominant staple food, rice is a vital source of nutrition, comprising proteins, lipids, essential vitamins (B and E), and minerals. Consequently, rice milling industry produces vast amounts of residue, known as rice husk (RH), which remains largely underutilized [2]. Similarly, the Pakistan's Sindh province is a major contributor to date fruit production, with the "Aseel" variety being the pre-dominant commercial and export cultivar [3]. Date seeds (DS), a common by-product, are typically utilized as animal feed or discarded as waste [4]. Among various biomass conversion technologies, pyrolysis has garnered significant attention for its ability to convert biomass into solid, liquid, and gaseous products under inert conditions. Zhang et al. [5] assessed the combined effects of acid washing and torrefaction on the kinetic parameters and product yields of RH using TGA and fixed-bed reactor. Kamruzzaman et al. [6] evaluated the suitability of various RH types for thermochemical conversion. El May et al. [7] conducted a kinetic analysis of the thermal decomposition behavior of several date palm residues including date seeds (DS), leaflets, rachis, trunk, and fruit stalks via thermogravimetric analysis. Focusing on product characterization, Bensidhom et al. [8] investigated the pyrolysis behavior and volatile composition of DS and date palm petiole using gas chromatography-mass spectrometry (GC-MS). Jamro et al. [9] demonstrated the potential for hydrogen production from date palm biomass via gasification technology. In another study, Bensidhom et al. [10] characterized the pyrolysis products of date palm waste, such as leaflets, empty fruit bunches, and glaich, using a fixed bed reactor.

Beyond conventional pyrolysis, the co-pyrolysis of multiple biomass feedstocks has emerged as a promising conversion pathway [11]. This approach has been explored using a variety of feedstock combinations. For instance, Tauseef et al. [12] investigated the co-pyrolysis of RH and coal, while Berthold et al. [13] examined the influence of different plastics on the co-pyrolysis of RH. Other studies have focused on enhancing product yields; Pan et al. [14] optimized syngas yield from the co-pyrolysis of RH and sewage sludge, whereas Fadhil and Kareem [15] reported increased bio-oil and biochar yields from date palm seeds and olive stones. Wang et al. [16] utilized TG-FTIR-MS techniques to investigate the co-pyrolytic behavior of RH and sewage sludge, finding that blending RH enhanced the degradation behavior of mixtures. Parthasarathy et al. [17] analyzed the physicochemical properties and thermo-kinetic behavior of date palm seed, camel dung, and their blend using thermogravimetric analysis. Inayat et al. [18] conducted co-pyrolysis of date palm seed and plastic waste in a fixed-bed reactor. Al-Rumaihi et al. [19] used the Aspen plus simulation model to study the co-pyrolysis of date seeds, camel manure, and low and high-density polyethylene, investigating the effect of mixing ratios on product yields. Alsulami et al. [20] focused on the characterization and thermo-kinetic analysis of the co-pyrolysis of DS, coffee grounds, and prickly pear wastes. Raza et al. [21] conducted co-pyrolysis of DS and cashew shell, with an emphasis on synergistic interactions, thermal degradation behavior, and thermo-kinetic analysis using TGA. Ibrahim et al. [22] studied the co-pyrolysis behavior of DS and pistachio shells. Despite these advancements, a notable research gap exits in the literature regarding the co-pyrolysis of rice husk (RH) and date palm seeds (DS), specifically concerning the influence of blending ratios and temperature on product yields and gas evolution.

This study experimentally investigated the co-pyrolysis of RH and DS, focusing on the influence of blending ratios (25:75, 50:50, 75:25) and temperatures (300, 400, 500, and 600 ºC) on product distribution. A key objective was to analyze the synergistic effects arising from the co-pyrolysis of these two biomasses.

1. Materials and Methods

2.1 Samples Preparation

Rice husk (RH) and date palm seeds (DS) were procured from a local rice mill and dates processing factory, respectively, both located in Therhi, Khairpur Mir's, Sindh, Pakistan. DS as received were washed with tap water to remove impurities, and both feedstocks were sun-dried for seven days to reduce moisture content. Subsequently, the materials were ground into a powder and sieved to a uniform particle size of 80 mesh (0.2 mm). Five distinct samples were prepared: two pure samples (100%RH and 100%DS) and three blended samples at weight ratios of 25:75, 50:50, and 75:25 (RH:DS). All prepared samples were stored in airtight containers to prevent moisture absorption prior to analysis.

2.2 Experimental methods

2.2.1 Pyrolysis product experiments

As presented in Fig .1, the pyrolysis experiments were conducted in a laboratory-scale horizontal fixed-bed reactor under an inert atmosphere. For each run, a 10 g sample was placed centrally within the tube, which was then sealed. The sample was heated from ambient temperature to the target pyrolysis temperatures (300, 400, 500, and 600 °C) at a constant heating rate of 20 °C/min, followed by a 20-minute isothermal hold. The condensable vapors were collected in an ice-water condenser, while non-condensable gases were captured in gas bags between 200 and 600 °C in gas bags for subsequent analysis. The yields of pyrolysis products (wt.%) were calculated using the following equations [23]:

$$\text{Biochar }(\%) = \frac{Y_{\text{solid}}}{m_i} \quad (1)$$

$$\text{Liquid }(\%) = \frac{Y_{\text{Liquid}}}{m_i} \quad (2)$$

$$\text{Gas }(\%) = 100 - (\text{Biochar} + \text{Liquid}) \quad (3)$$

where, m_i is the initial mass of the sample, Y_{solid}, Y_{Liquid} represent solid and liquid yields respectively. The composition of non- condensable gases was analyzed using a gas chromatograph. The volumetric yields (Y_x) of the gas components were calculated of various gas components using this relation [24]:

$$Y_x = \frac{V_{N_2}}{C_{N_2}} \times \frac{C_x}{m_s} \quad (4)$$

Here, V_{N2}, C_{N2}, C_x and m_s are the volume of nitrogen, volumetric concentration of nitrogen, volumetric concentration of gas component and sample mass respectively.

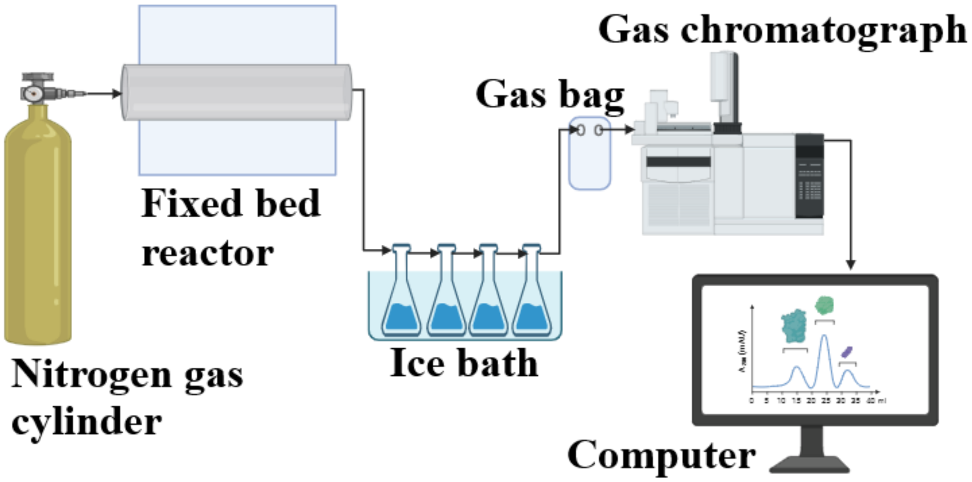

Fig. 1. Schematic diagram of the experimental setup.

3. Results and discussions

3.1. Effect of temperature on product yields

Pyrolysis experiments were conducted from 300 to 600 °C at a heating rate of 20 °C/min. The distribution of pyrolysis products for 100%RH and 100%DS across this temperature range is presented in Fig. 2. For all feedstocks, biochar yield exhibited a consistent decrease with increasing temperature, attributed to the more extensive decomposition of the biomass at higher temperatures. Consequently, lower temperatures are more favorable for maximizing biochar production. Notably, the highest biochar yield was achieved by 100%RH at 300 °C. The elevated biochar yield from 100%RH can be attributed to its higher AC. A similar decreasing trend in biochar yield with rising temperature was also observed for 100%DS (Fig 2 (b)). The biochar yields obtained at 300 °C for both feedstocks are consistent with literature values, such as 48% for water hyacinth [25] and 44.32-51.36 % for various agricultural straws [26]. In contrast to biochar, the liquid yield exhibited a distinct behavior, reaching a maximum at an intermediate temperature before declining. For 100%RH, the liquid yield increased from 300 °C to a peak of 35.35% at 500 °C, consistent with findings from Hassan et al. [27] and Tang et al. [28]. For 100%DS, the maximum liquid yield of 48.59 % was reached at a lower temperature of 400 °C, which aligns with the results of Jin et al. [25]. The subsequent decrease in liquid yield at higher temperatures is attributed to the secondary cracking of vapors into gaseous products. The higher liquid yield observed for 100%DS, compared to 100%RH, is likely due to its higher volatile matter and lower ash content. The variation in liquid yield between RH and DS could be due to differences in their composition.

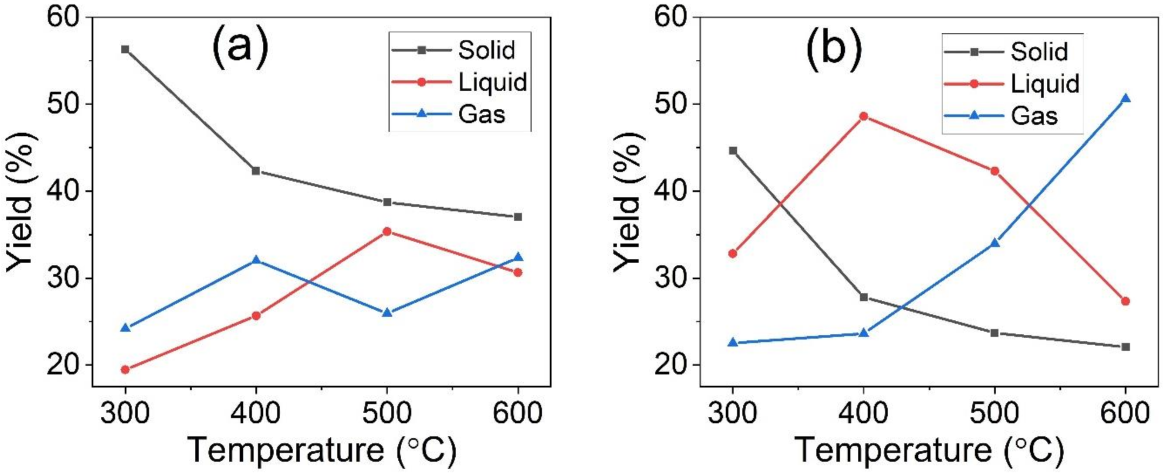

Fig. 2. Effect of pyrolysis temperature on product yields (a) 100%RH, (b) 100%DS

3.2. Effect of blending ratio on co-pyrolysis product yields

Fig. 3 illustrates the influence of various blending ratios on product yields at various pyrolysis temperatures. At 300 ºC, solid yields were highest across all blends, particularly for the 25%DS+75%RH blend, suggesting limited thermal decomposition. As the proportion of DS increased, solid yield decreased while liquid yield increased. Gas yield was the lowest overall, though slightly higher in the 75%DS+25%RH blend. At 400 ºC, solid yield declined compared to 300 ºC but remained significant in the 25%DS+75%RH blend. Gas yield increased noticeably from 300 ºC, peaking in the 75%DS+25%RH blend. At 500 ºC, solid yield continued to decrease, reaching its lowest value in the 75%DS+25%RH blend. Liquid yield peaks in the 75%DS+25%RH blend, indicating enhanced liquid formation at this temperature. In contrast, gas yield decreased as the DS proportion increased. At 600 ºC, both solid and liquid yields decreased further across all blends, while gas yield increased substantially.

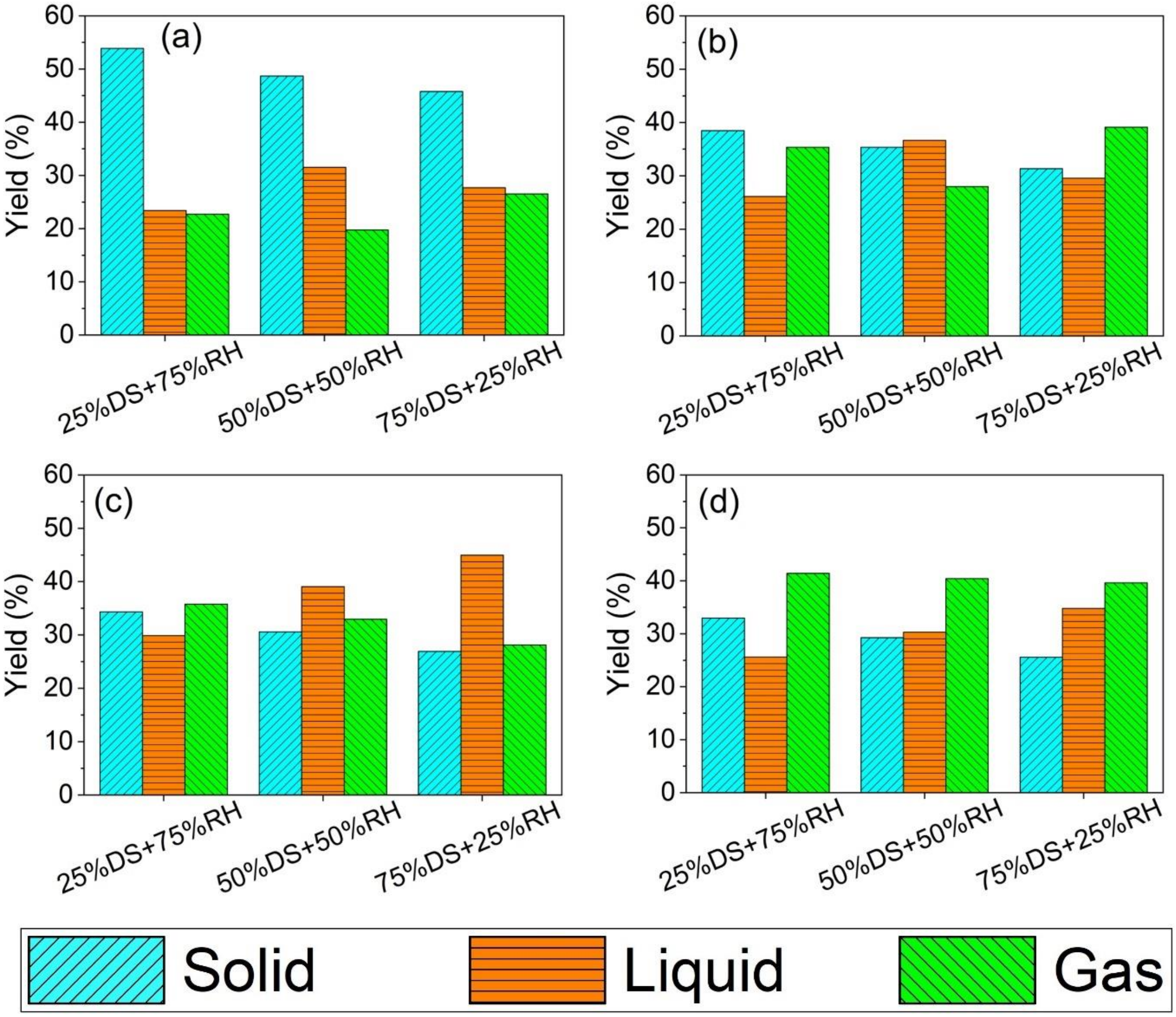

Fig. 3. Effect of various blending ration on product yields at various temperatures. (a) 300 ºC, (b) 400 ºC, (c) 500 ºC, and (d) 600 ºC.

3.3. Synergistic interactions

The synergistic effect was evaluated by calculating the difference (ΔY) between the experimental and theoretical yields at various blending ratios and pyrolysis temperatures. The calculation was based on using the following equations [29].

$$\Delta Y = Y_{\text{exp}} - Y_{\text{cal}} \quad (5)$$

$$Y_{\text{cal}} = x_{\text{DS}} Y_{\text{DS}} + x_{\text{RS}} Y_{\text{RS}} \quad (6)$$

where Y_{DS} and Y_{RS} represent the experimental product yields of the 100%DS and 100%RS samples, respectively, and x_{DS} and x_{RS} denote the initial weight percentages of DS and RS in the blends.

At 300 ºC, ΔY for solid yield was negative across all blends except for the 25%DS+75%RH blend. Similarly, ΔY for liquid yield was negative in the 75%DS+25%RH blend. At 400 ºC, ΔY for solid yield was negative in both the 25%DS+75%RH and 75%DS+25%RH blends, while ΔY for liquid yields was negative across all blends. At 500 ºC, ΔY for solid yield was negative across all blends, whereas ΔY for liquid yield was positive for the 50%DS+50%RH and 75%DS+25%RH blends. At 600 ºC, ΔY for solid yield remained negative across all blends, and ΔY for liquid yield was negative only in the 25%DS+75%RH blend. These deviations highlight the importance of interaction effects during co-pyrolysis.

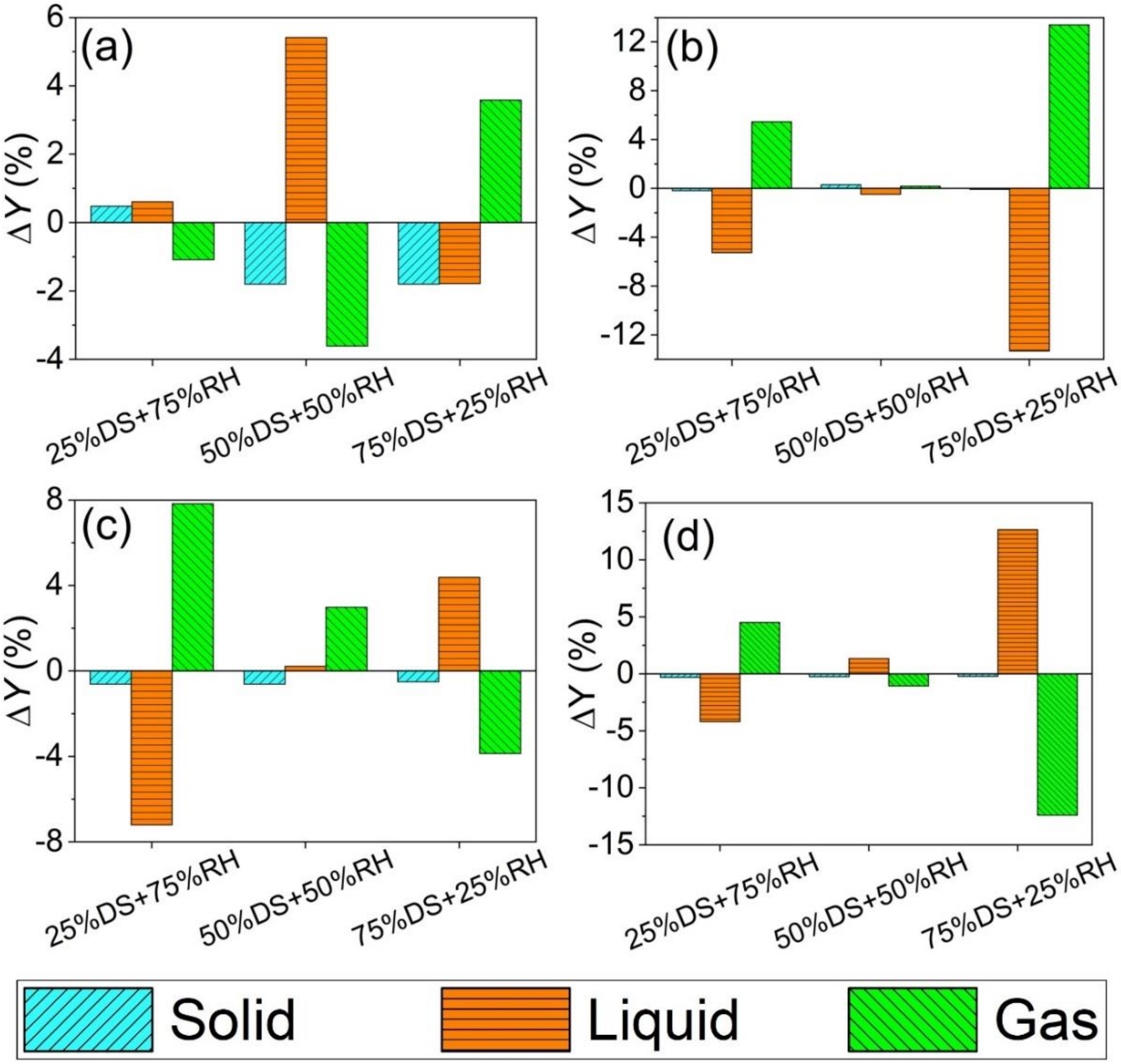

Fig. 4. The deviations in product yields at various blending ratios and pyrolysis temperatures (a) 300 °C, (b) 400 °C, (c) 500 °C, and (d) 600 °C.

3.4. Gas evolution

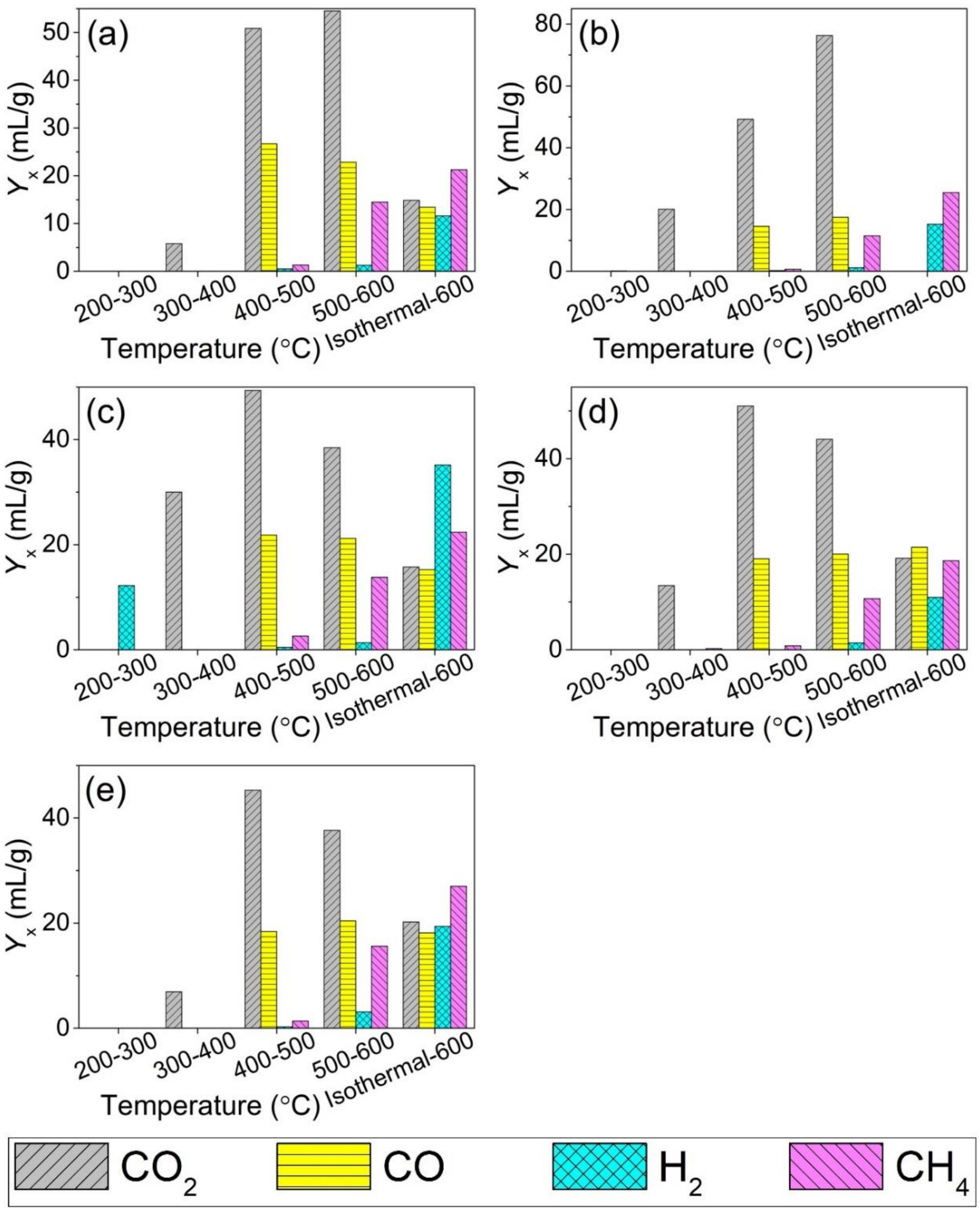

Fig. 5. Gases evolution of all individual and blended samples (a) 100%RH, (b) 100%DS, (c) 25%DS+75%RH, (d) 50%DS+50%RH, and (e) 75%DS+25%RH.

Evolved gases, collected in gas bags, were analyzed using gas chromatography. CO_2 yields for both 100%RH and 100%DS samples peaked at 500-600 °C. In contrast, CO_2 yields from all blends reached their maximum within the temperature range of 400-500 °C range. H_2 and CH_4 yields increased with rising temperature across all samples. The 25%DS+75%RH blend exhibited a higher CO yield than the 100%DS sample across all temperatures. During the isothermal stage, the 50%DS+50%RH and 75%DS+25%RH blends produced greater CO yields than individual samples. All blends generated higher H_2 yields than the individual samples at 500-600 °C, with the 25%DS+75%RH and 75%DS+25%RH blends exceeding the individual samples during the isothermal stage. Additionally, the 25%DS+75%RH and 75%DS+25%RH blends showed elevated CH_4 yields compared to the individual samples in the 400-500 °C range, with the 75%DS+25%RH blend showed the highest CH_4 yield compared to individual samples during the isothermal stage.

4. Conclusions

This study investigated the influence of blending ratio and temperature on product distribution during the co-pyrolysis of rice husk (RH) and date palm seed (DS) using a fixed-bed reactor. Gaseous products were analyzed using gas chromatography. The solid yields consistently decreased over the entire temperature range (300 to 600 °C) for all biomass feedstocks, likely due to the progressive decomposition of biomass at higher temperatures. Therefore, lower temperatures are favorable for maximizing biochar yield. The liquid yield for 100%RH was found to increase to 35.35% from 300 to 500 °C, with the maximum yield observed at 500 °C. At higher temperatures, the liquid yield decreased. For 100%DS, the liquid yield increased up to 400 °C, reaching a maximum of 48.59% at this temperature, and then decreased at higher temperatures. Increasing the DS proportion decreased in char and gas yields while increasing liquid yield, with the maximum liquid yield observed at 75% DS. The solid yield exhibited a negative deviation, while the liquid yield showed a positive deviation across most temperatures and blending ratios. Thus, the co-pyrolysis of RH and DS reduced the char yield and promoted the formation of bio- production. CO_2 yields from all blends were maximum in the temperature range of 400-500 °C. H_2 and CH_4 yields increased with temperature for all samples. The 25%DS+75%RH blend exhibited higher CO yield than the 100%DS sample across all temperature ranges. The 50%DS+50%RH and 75%DS+25%RH blends showed higher CO yields than the individual samples during the isothermal stage. All blended showed higher H_2 yields than the individual samples at 500-600 °C, with the 25%DS+75%RH and 75%DS+25%RH blends exceeding the individual samples during the isothermal stage. The 25%DS+75%RH and 75%DS+25%RH blends also had higher CH_4 yields than individual samples in the 400-500 °C range, and the 75%DS+25%RH blend showed the highest CH_4 yield compared to individual samples during the isothermal stage.

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