Chapter 5

Influence of operational parameters on co-gasification process

5.0. Introduction

Gasification is a thermochemical conversion technique that transforms carbon-rich materials, such as biomass, coal, and petroleum coke (petcoke), into combustible and non-combustible gases. This process generates synthesis gas, in addition to other fuels and chemicals. Optimizing various operational parameters, including the gasification medium, catalyst, pressure, temperature, heating rate, and residence time, is essential to achieve an effective gasification process. Using CO_2 as a gasification medium offers several advantages. It serves as a carbon source and an oxidant in multiple chemical reactions, facilitating the efficient conversion of carbon-based materials [166]. Furthermore, employing CO_2 in gasification can help reduce greenhouse gas emissions and enhance carbon monoxide production through the Boudouard reaction, as shown in the equation below [81, 167]. This method has shown promising results and has the potential to address several environmental challenges.

$$\mathrm{C} + \mathrm{CO_2} \leftrightarrow 2\mathrm{CO} \qquad + 172\ \mathrm{kJ/mol}$$

A study conducted by Szul *et al.* (2021) highlighted that the presence of CO_2 significantly impacts both hydrogen (H_2) yield and temperature distribution in pressurized gasification systems [81]. This influence increases carbon monoxide (CO) production and enhances carbon conversion efficiency. Similarly, research by Stec *et al.* (2018) observed that CO yield also increases due to the influence of CO_2 [166].

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Furthermore, Kwon *et al.* (2012) observed that using CO_2 during gasification improves carbon conversion and reduces tar formation through an accelerated cracking mechanism [168]. Gasification occurs at temperatures greater than 973 K in environments controlled by temperature, pressure and gasification medium such as air, CO_2, O_2, and/or steam [29]. During the biomass gasification process, 63-75 wt% of the biomass is converted into syngas, while the remaining 25-37 wt% is transformed into carbonaceous solid residues (char and soot particles) and condensable products, including tars (1-10 wt%). Despite its potential, the industry faces several challenges with the large-scale uses of biomass. These include low energy density and issues related to corrosion, slagging, and fouling caused by the high Alkali and Alkaline Earth Metals (AAEMs) in biomass. However, these challenges can be mitigated by co-gasifying biomass with petcoke. The co-gasification process leverages the high AAEM content in biomass, which acts as a natural catalyst, leading to improved gasification efficiency. Combining these two fuels can address the limitations of each gasification feedstock [100, 169]. Carbon dioxide (CO_2) can be utilized as a gasification medium for efficient co-gasification, while alkali carbonate salts act as catalysts. The catalyst concentration increases as carbon decomposition occurs during catalytic gasification, leading to higher specific reaction rates. These reaction rates are calculated to assess the change in rate per unit mass of the reactants or products. Furthermore, the catalysts create pits and channels within the carbon structure, enhancing the accessibility of active and reactive sites for gasification reactions [95]. Edreis *et al.* (2017), (2018) conducted a study on the CO_2 co-gasification of petcoke with various biomass materials using a thermogravimetric analyzer [170, 171]. The study found that adding biomass to petcoke during the CO_2 gasification process significantly enhanced the reactivity of petcoke. This established the existence of a synergistic effect resulting from the blending of these materials. The observed synergistic effect during gasification arises from the significant release of volatile matter due to the thermal breakdown of the weakest covalent bonds in the organic matter. As a result, a high number of free radicals are generated from the degradation of biomass. These radicals interact with the organic components of biomass and potentially promote decomposition and gasification reactions in petroleum coke.

The present study aims to understand the effects of different pressures and temperatures on the CO_2 gasification of bamboo char impregnated with K_2CO_3 and its blend with petcoke. Unlike previous studies that primarily used thermogravimetric analysis (TGA), this research includes laboratory and pilot-scale gasifier experiments, highlighting the potential for sustainable energy generation and CO_2 recycling [172 - 174]. Additionally, Fourier-transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray analysis (EDX) are used to evaluate the morphological structure and composition of both raw bamboo and its char. This comprehensive approach provides a detailed understanding of the chemical and physical transformations during pyrolysis and catalyst impregnation, supplementing the gasification experiments with material analysis and experimental results.

5.1 Results and discussion

5.1.1 Feedstock characterization

5.1.1.1 Elemental and mineral composition

The Energy Dispersive X-ray (EDX) analysis revealed changes in the elemental composition of bamboo char due to the impregnation with the K_2CO_3 catalyst. Fig. 5.1 and 5.2 indicate a significant increase in potassium content on the surface of the char particles. Initially, the potassium content in bamboo char was approximately 42.68 %, which could enhance gasification by creating pores on the surface [173]. After the impregnation with K_2CO_3, the potassium content increased to 77.51 %, which promotes the water-gas shift reaction during the gasification process [83]. In addition, the analysis of K_2CO_3-impregnated char revealed a reduction in silicon (Si) and aluminum (Al) levels. This reduction is significant because both silicon and aluminum can hinder the conversion of char, making it less reactive by forming inactive compounds with other ash elements. High concentrations of silicon in biomass can lead to the formation of molten ash layers that can encapsulate char particles and restrict the supply of oxidant gases, thereby reducing char conversion [171]. Overall, these changes could enhance the efficiency of converting biomass into valuable products, presenting opportunities across various applications.

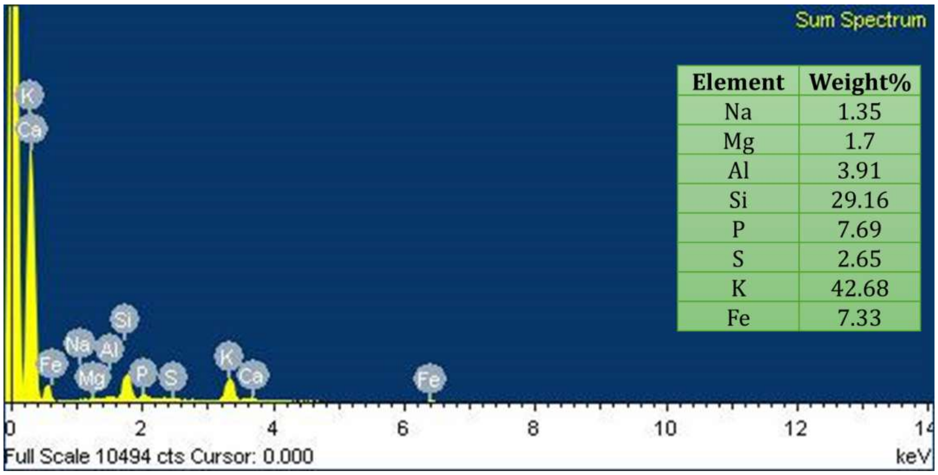

Fig. 5.1 EDX elemental analysis and mapping of bamboo char without catalyst loading

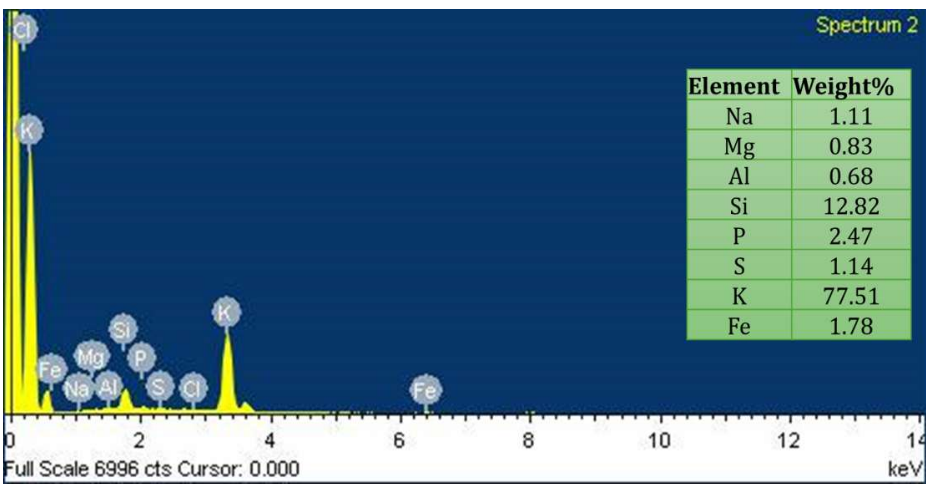

Fig. 5.2 EDX elemental analysis and mapping of K_2CO_3 impregnated bamboo char

5.1.1.2 Surface morphology by FESEM analysis

Fig. 5.3 presents FESEM images of raw bamboo, bamboo char, and K_2CO_3-impregnated bamboo char, all produced under atmospheric pressure at a temperature of 973 K. The raw bamboo exhibits long, fibrous structures and some microfibers, but it lacks the necessary pores for effective gas-solid reactions during char gasification. After the pyrolysis process, these fibrous structures disappear, and porous structures emerge, potentially increasing the surface area available for reactions, as shown in Fig. 5.3(b) [176]. This change in the internal structure of the char is due to thermal decomposition and the release of volatile compounds, which create distinct channels and pores. Similar porous char structures have been noted in studies involving various biomass sources and pyrolysis temperatures, supporting the findings of this research [177].

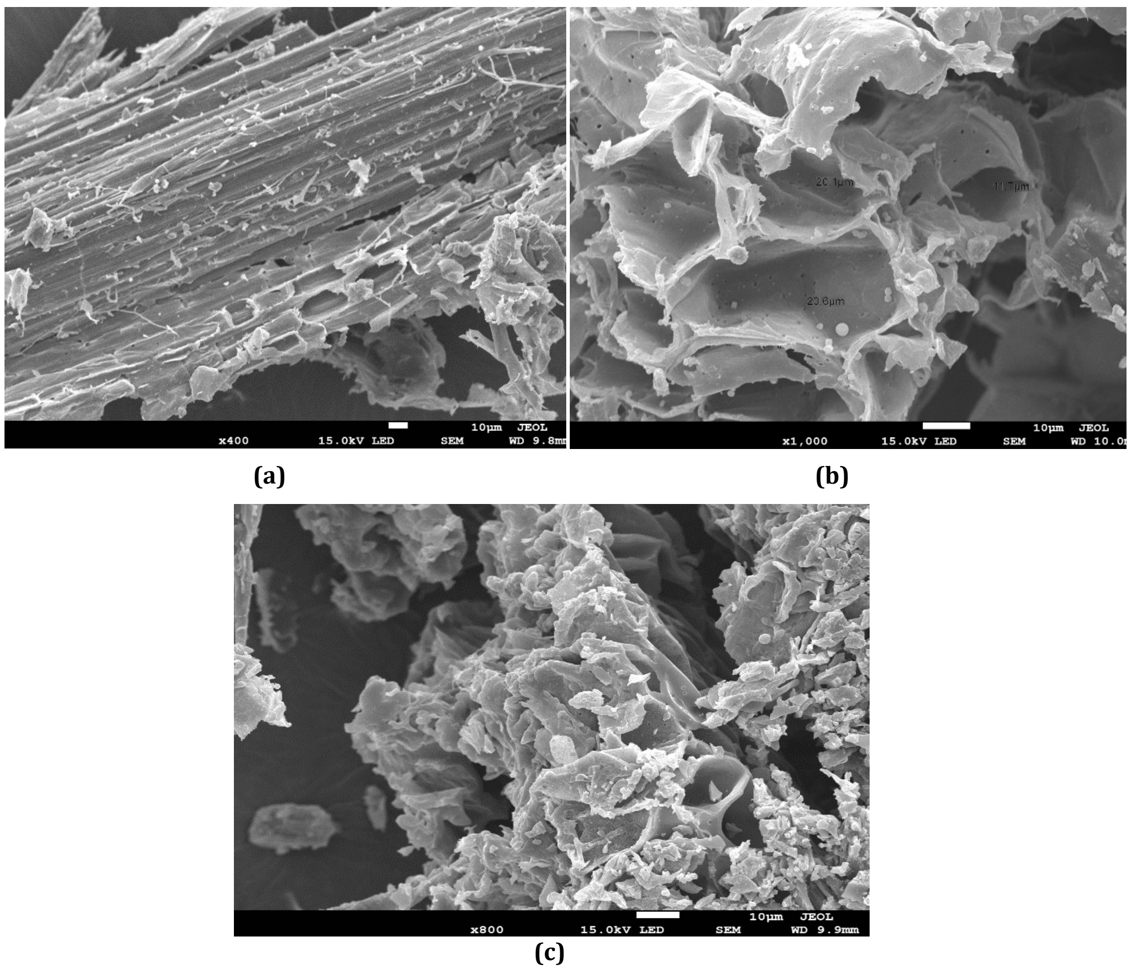

Fig. 5.3 FESEM images (a) raw bamboo, (b) bamboo char and (c) K_2CO_3 loaded bamboo char

Fig. 5.3(c) illustrates the well-developed pore distribution present in the K_2CO_3-impregnated bamboo char. This pore structure is likely a result of the dispersion of the catalyst across the char surface or within its cellulosic internal structure during the wet impregnation process. When subjected to a temperature of 973 K, a reaction occurs between the bamboo char and K_2CO_3, potentially facilitating the intercalation of metallic potassium (K) into the carbon sheets. This interaction is expected to significantly enhance porosity of the char samples. Additionally, the removal of tarry particles from the pores can lead to the formation of both micropores and mesopores [178]. The resultant increase in porosity and surface area of the bamboo char, now loaded with the catalyst, provides a more extensive surface area, which is advantageous for promoting efficient and extensive gasification reactions.

5.1.2 Effect of catalyst impregnation on bamboo char during CO_2 gasification

The natural surface chemistry of char may not always be sufficient to facilitate efficient heterogeneous reactions between carbon and gas during gasification. This is where alkali and alkaline earth metal compounds (AAEMs) serve as catalysts, enhancing the physicochemical properties of char, making it more reactive through the integration of functional groups. These functional groups act as active sites for solid-gas reactions. In this experiment, K_2CO_3 is used as a catalyst, playing a significant role in char gasification. Fig. 5.4 illustrates that the CO mole fraction curve during CO_2 gasification of K_2CO_3-impregnated bamboo char differs from that of bamboo char without catalyst at atmospheric pressure (1 atm) at temperatures of 1023 K, 1123 K, and 1173 K. At all temperature ranges, the yield of CO mole fraction during CO_2 gasification of K_2CO_3-impregnated bamboo char is higher than that of bamboo char without a catalyst. This indicates that potassium catalyses oxygen from CO_2 and transfers it to the surface, which promotes a reaction with carbon to generate CO. The concentration of CO rises to a peak before decreasing until it reaches a plateau at higher temperatures of 1123 K and 1173 K. Prat *et al.* (2020) reported similar findings [179]. Potassium plays a catalytic role by extracting oxygen from CO_2 and transferring it to a surface, facilitating a reaction with carbon to produce CO. The concentration of CO initially increases to a peak, then decreases until it stabilizes at higher temperatures of 1123 K and 1173 K. Temperature and pressure are crucial factors in the gasification process, as they significantly impact conversion rates and the generation of products during thermochemical reactions. The extent of their influence can vary depending on the specific reaction, the reactants involved, and the conditions under which the reaction occurs. Higher system temperatures enhance product generation, especially in endothermic reactions like the Boudouard reaction. According to Le Chatelier's Principle, increasing the temperature favors the formation of products, while decreasing the temperature inhibits it due to the endothermic nature of the Boudouard reaction.

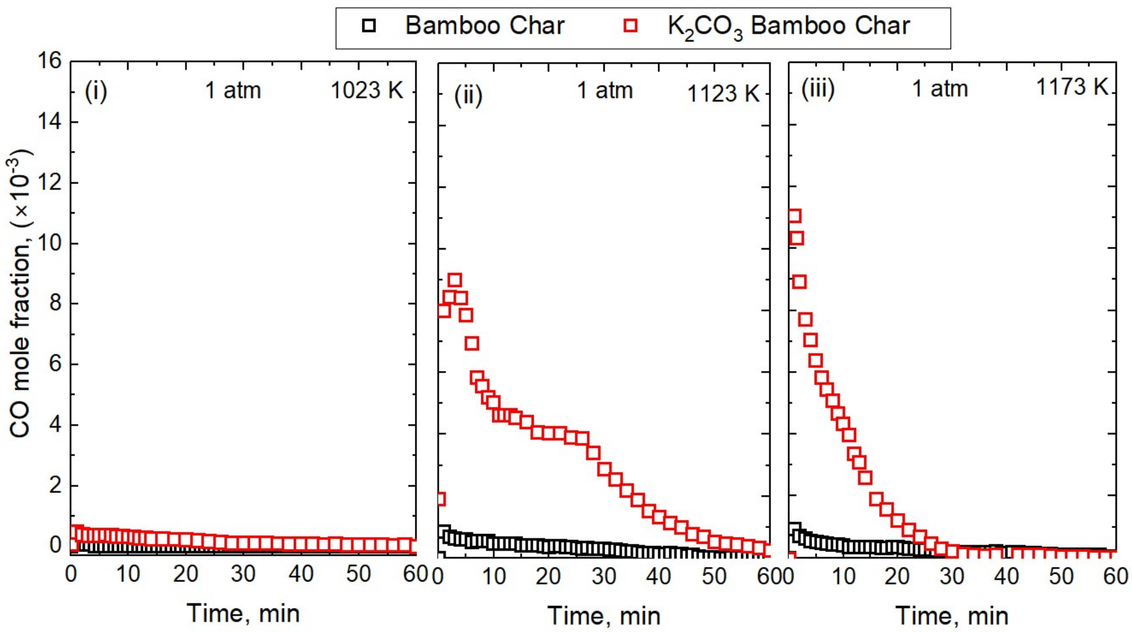

Fig. 5.4 Influence of catalyst loading on bamboo char during CO_2 gasification

5.1.3 Effect of temperature and pressure on K_2CO_3 impregnated bamboo char gasification

Fig. 5.5 illustrates the relationship between the carbon monoxide (CO) mole fraction and time during the gasification of K_2CO_3-impregnated bamboo char using carbon dioxide (CO_2). The results indicate that increasing pressure and temperature leads to a higher yield of CO. Specifically, as the temperature rises from 1023 K to 1123 K at 1 atm of pressure, the yield of CO increases. Temperature plays a critical role in accelerating reaction rates by providing additional energy to reactant molecules, resulting in more frequent collisions that facilitate the formation of the desired products due to the significant rise in energy levels. Additionally, higher temperatures can lower the activation energy barrier, enabling more reactant molecules to overcome this barrier and form the desired products. Increasing the temperature from 1123 K to 1173 K at a pressure of 1 atm significantly increases the concentration of carbon monoxide (CO). Moreover, increasing the pressure from 1 atm to 3 atm during the gasification process enhances CO concentration. This trend of increasing CO yield is consistent across all temperature ranges when the pressure is maintained at 3 atm.

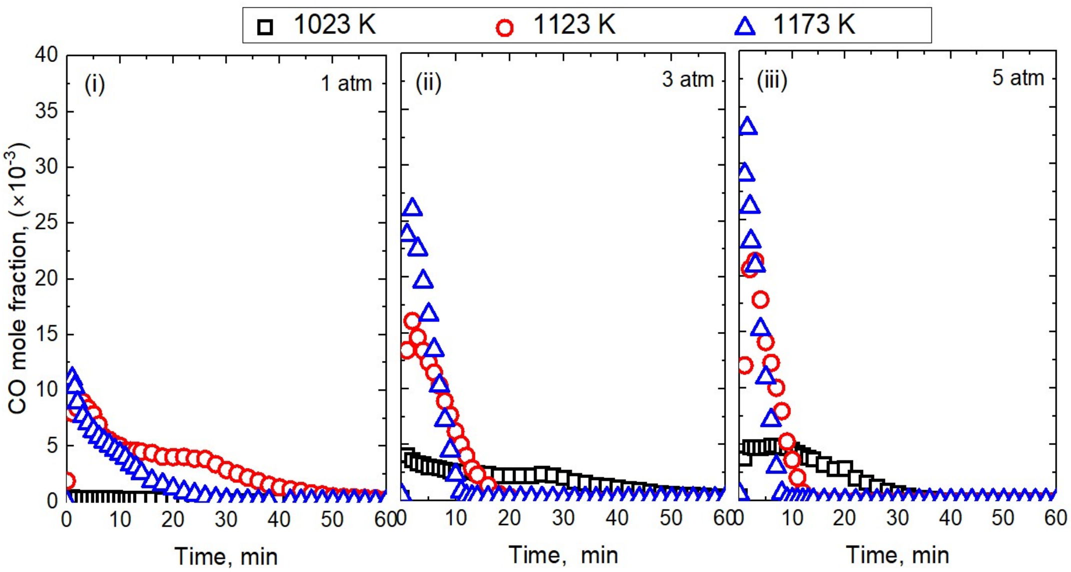

Fig. 5.5 CO mole fraction for different gasification temperatures and pressures

Increasing the pressure from 3 to 5 atm led to a significant increase in CO mole fractions. The higher compression in the gas-phase reaction resulted in higher concentrations of reactant molecules, which allowed for more frequent collisions. This favored the reaction pathway and enhanced the formation of specific products. Pressure has a dominant role than temperature in gas-phase reactions, particularly those involving changes in the number of gas molecules. This finding is consistent with previous studies by Roncancio *et al.* (2024), and Sircar *et al*. (2014) [180, 181]. The study revealed that the concentration of CO varied depending on the physical and chemical properties of the biomass sample and the catalyst used. Fig. 5.5 presents that at 1 atm pressure, the CO mole fraction peaks within 1 minute across all temperature ranges. As the pressure increases from 1 atm to 3 atm, it takes approximately 2 minutes to reach the peak CO concentration. Even at a pressure of 5 atm, the time required to achieve the peak CO mole fraction remains relatively similar. The impact of increasing pressure on CO formation is complex, likely influenced by increased temperature and increased concentration of active sites. Moreover, the time required to reach the plateau decreases with an increase in temperature, regardless of the pressure applied. This suggests that temperature significantly influences the reaction rate and the amount of CO produced, illustrating that higher temperature increases the kinetic energy of the molecules and provides the necessary activation energy for the reaction to proceed. Fig. 5.6 presents the percentage of char conversion for K_2CO_3-impregnated bamboo char during CO_2 gasification at different temperatures and pressures. At a lower temperature of 1023 K and atmospheric pressure, the char was gradually consumed, reaching a plateau at a conversion rate of about 10%. In contrast, at higher temperatures of 1123 K and 1173 K at the same pressure, the conversion percentage increased to approximately 50 %. This suggests that some char remained unconverted at 1 atm and 1023 K temperature.

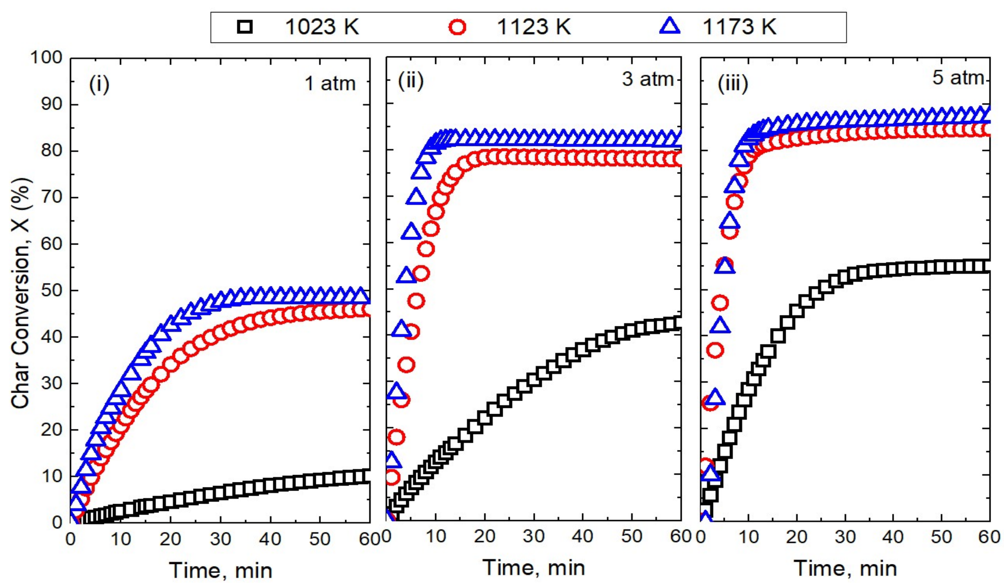

Fig. 5.6 Char conversion of K_2CO_3 loaded bamboo chars during CO_2 gasification at varying temperature and pressure

Increasing the pressure from 1 to 3 atm and subsequently to 5 atm resulted in higher char conversion across all temperature ranges. This improvement is due to the increased concentration of CO_2 around the char particles, which enhances diffusion into the porous char structure. This increased CO_2 diffusion is critical as it accelerates the gasification reaction, promoting a higher rate of char consumption. Under such condition, the char conversion percentage achieved the 80% threshold, which is considered essential for efficient gasification in various engineering applications [171]. The increased pressure not only enhances the rate of reaction but also ensures that the char undergoes sufficient transformation. However, at high pressures, certain catalytic compounds, such as potassium, may undergo undesirable changes, including agglomerate and melt. This can result in the blockages of pore, which negatively affect the overall gasification process by restricting the accessibility of the reactive surface area. Consequently, despite the advantages of higher pressure for gasification efficiency, excessive pressure can eventually lead to a decrease in char conversion due to the blockage of pores.

5.1.4 Effect of blending petcoke with K_2CO_3-impregnated bamboo char

The present study investigates the synergistic effect observed during the CO_2 gasification of bamboo char impregnated with K_2CO_3, blended with petcoke. The result obtained from the gasification of K_2CO_3-impregnated bamboo char (referred to as B100P0) serve as a baseline for comparison with the petcoke-blended samples. However, establishing a baseline for petcoke alone is challenging due to its inherently low volatile content (9.87%) and low reactivity, which limits its effectiveness in gasification processes. Therefore, blending petcoke with biomass or biochar is recommended for CO_2 gasification applications. The study examined the blends B100P0, B80P20, B60P40, and B50P50 for the experiments. In the gasification experiments, the amount of carbon monoxide (CO) produced is measured at a constant temperature of 1173 K under two different pressure conditions: 1 atm and 3 atm (see Fig. 5.7). When blending 80% and 60% potassium carbonate (K_2CO_3)-impregnated bamboo char with petcoke, the resulting CO mole fraction remains nearly identical at 1173 K and 1 atm pressure. This indicates that at these specific conditions, the catalytic activity of the K_2CO_3-impregnated bamboo char plays a significant role in driving CO production, maintaining a consistent reaction outcome despite the differing char content. However, when the percentage of bamboo char is reduced by just 10%, creating a 50% bamboo char and petcoke blend, there is a decrease in the CO mole fraction. This suggests that the specific composition of the char-petcoke blend is critical for optimal catalytic activity and CO production. A similar trend is observed in the char conversion rates, as shown in Fig 5.8, where the conversion rates are around 40 % for the B80P20 and B60P40 blends, reflecting efficient char reactivity. In contrast, the B50P50 blend exhibits a notable decrease in conversion efficiency, with rates dropping to 25 %. The decline in conversion rates may be due to a decreased reactive surface area and catalytic potential of the bamboo char when its proportion in the blend is reduced. This reduction limits its overall effectiveness in gasification reactions.

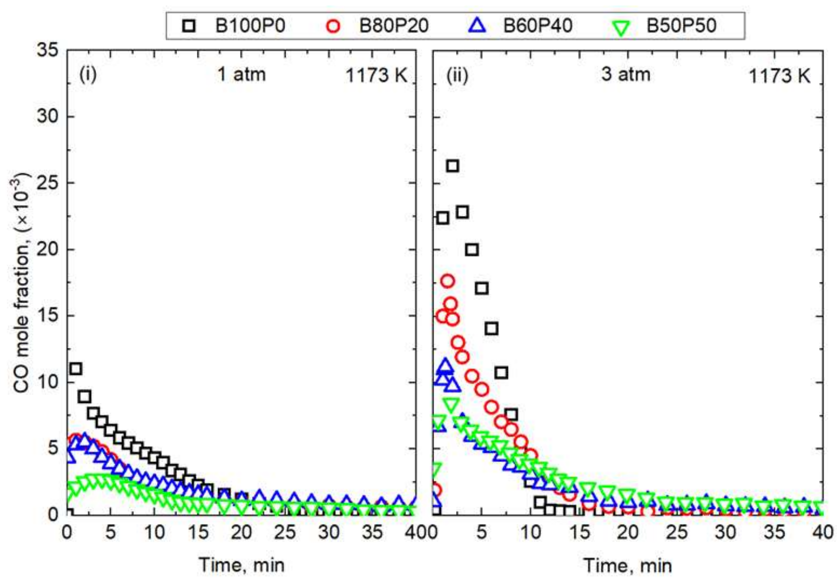

Fig. 5.7 CO mole fraction under CO_2 gasification of various blends with K_2CO_3 loaded with bamboo char at constant temperature and varying pressure

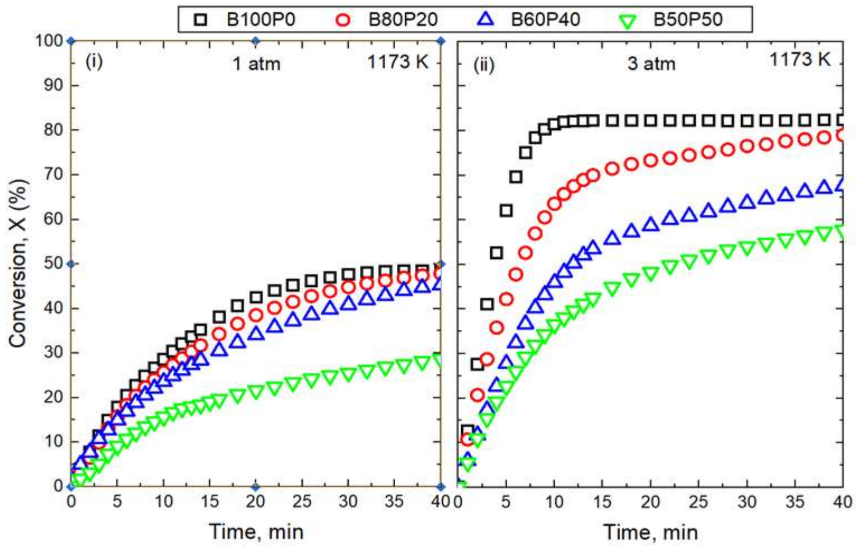

Fig. 5.8 Char conversion of petcoke with K_2CO_3 loaded with bamboo char at constant temperature and varying pressure during CO_2 gasification

As illustrated in Fig. 5.7 and 5.8, increasing the pressure from 1 atm to 3 atm significantly enhanced both the CO mole fraction and char conversion rates. At a constant temperature of 1173 K, the peak CO mole fraction for the B80P20 and B60P40 samples increased when the pressure is raised to 3 atm. Under these conditions, the char conversion percentages reached between 65 % and 75 % for both B80P20 and B60P40 samples. This increase in CO mole fraction and char conversion is largely attributed to the catalytic effects of alkali metals present in the bamboo char. The transfer of alkali metals between particles within the char is important as it enables these metals to move from the char to the petcoke. This movement weakens the carbon-carbon (C–C) bonds in the char, thereby enhancing the reaction rate between the char and CO_2. Consequently, the percentage of bamboo char in the blend significantly affects its catalytic effectiveness during CO_2 gasification.

5.2 Summary

The present study investigated the interaction between the catalyst and char during CO_2 gasification using bamboo char impregnated with K_2CO_3. It examined how variations in temperature and pressure could enhance the gasification process and the effects of blending petcoke with K_2CO_3-loaded bamboo char. The findings revealed that adding K_2CO_3

significantly improved the gasification process compared to un-impregnated char, as evidenced by an increased yield of the CO mole fraction. The interaction between the potassium catalyst and the char particles became more pronounced at elevated temperatures. Furthermore, using a catalyst decreased the concentrations of silicon (Si) and aluminum (Al) in the char, which typically hinder gasification by forming alumino-silicates. Higher temperatures lowered the energy barrier for gasification, leading to increased carbon monoxide (CO) production. Furthermore, high-pressure conditions enhanced CO generation. The conversion and reactivity of the char are mainly affected by temperature and pressure. Increased pressure resulted in a higher concentration of reacting gases, which improved diffusion into the porous char structure and enabled complete conversion and consumption of the char. The study found that increasing the percentage of K_2CO_3-loaded bamboo char in the petcoke blend while raising the reaction pressure at a constant temperature of 1173 K improved carbon monoxide (CO) generation and char conversion. The optimal ratios for maximizing the catalytic effect are 80 % bamboo char with 20 % petcoke and 60 % bamboo char with 40 % petcoke.