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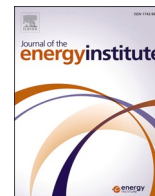
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Coke-free conversion of benzene at high temperatures

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ABSTRACT

This study investigates the conversion of benzene in a novel highly non-porous γ -Al₂O₃ packed bed reactor at 1000–1100 °C. The influences of packed bed presence, reforming medium (steam and CO₂), gas flow rate and benzene concentration on steady state benzene conversion are examined. In presence of packed bed, benzene conversions of 52, 75, and 84% were achieved with combined steam and CO₂ reforming at 1000, 1050, and 1100 °C, respectively. Whereas, benzene conversion of 65% without the packed bed at 1000 °C experienced a continuous increase in differential upstream pressure (DUP) of high temperature (HT) filter at reactor downstream due to deposition of in situ generated coke. High concentrations of generated CO and H₂ of 2.3 and 6 vol% with packed bed than 1.4 and 4.7 vol% without the packed respectively, were achieved. CO₂ reforming achieved high benzene conversions of 68–98% than 42–80% achieved with steam reforming at packed bed reactor temperatures of 1000–1100 °C. The results indicated that presence of γ -Al₂O₃ packed bed with possible surface reactions directed the conversion of benzene to combustible gases instead of coke. Hence, γ -Al₂O₃ packed bed reactor could be a suitable choice for coke-free conversion of tar of gasifier producer gas.

1. Introduction

Biomass represents a rapidly emerging renewable resource for the sustainable production of energy and value-added chemicals through its gasification [1]. Owing to continuously increasing global energy demand, it is a suitable choice with comparatively lower greenhouse gas emissions than with fossil fuels [2,3]. Biomass can be processed using thermal, biological, and physical methods. Thermal approach for biomass conversion such as gasification is one of the most prominent and efficient technologies for generating producer gas [4]. The producer gas can either be used for combined heat and power generation or be upgraded to various synthetic fuels and valuable chemicals [5,6]. However, the unwanted tar inevitably produced during biomass gasification is a major problem associated with this technique [7]. Tar is a mixture of condensable aromatic compounds that condense and polymerize in complex structures at cold spots in downstream equipment causing fouling, plugging, and even breakdown [8,9]. The usual high tar concentration in producer gas (i.e., 5–100 g/Nm³) must be decreased to 20 mg/Nm³ for useful applications [10]. The main ex situ producer gas-cleaning techniques for removing tar downstream from the gasifier are categorized as mechanical, catalytic and thermal methods [11,12]. Mechanical methods (e.g., using cyclones, filters, and scrubbers) can completely remove the tar. Because the tar fraction retains

approximately 10% of the energy of raw producer gas from indirect fluidized bed gasification, mechanical methods appear energy inefficient [13,14]. Catalytic and thermal tar cracking methods are the most commonly used approaches, as they convert the tar fraction into synthesis gas, increasing the overall energy content of the producer gas [13, 15]. The catalytic approach uses various organometallic/transition metals-based compounds and natural minerals (e.g., dolomite, calcined rocks, iron ores, zeolite, and olivine) for tar conversion. However, these catalysts experience deactivation due to coke, generated through tar polymerization [16].

The traditional approach of thermal tar cracking has been extensively used to significantly reduce the tar content at high temperatures and long residence times. Gilbert et al. [17] identified thermal homogenous conversion as the main route for converting the tar fraction of woody pyrolysis gas during a tar reforming investigation in a tubular reactor with/without a char bed. The tar content was significantly reduced from 37.6 to 15.3 wt% with an increase in temperature from 500 to 800 °C in the tubular reactor without the char bed. However, heavy tars, formed through secondary and tertiary reactions at increased temperatures, were resistant to cracking and required the injection of a gasifying agent (i.e., steam or steam/O₂). Wu et al. [18] investigated the formation and destruction of pyrolysis tar under thermal conditions at high temperatures of 700–1100 °C in a continuous reactor. Under inert

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thermal cracking conditions, the formation of combustible gases (e.g., CH_4 , CO , and H_2) increased with increased temperature due to the increased cracking of pyrolysis tar. However, O-containing or substituted one-ring aromatics were converted into polyaromatic hydrocarbons (PAHs) at higher temperatures. Zhai et al. [19] investigated the high temperature (900–1200 °C) thermal cracking of rice husk pyrolysis tar in a two-stage fixed bed pyrolysis system. Increasing the temperature reduced the tar content from 800 mg/kg of dry rice husk at 1000 °C to 18 mg/kg at 1200 °C. However, the concentration of PAHs generated due to secondary reactions of pyrolysis tar increased with increasing temperature. Wongchang et al. [20] analyzed the yield and structural characteristics of wood pyrolysis tar under high temperature thermal conditions (700–1200 °C). A similar tendency for decreasing tar concentration with increasing temperature reduced the tar concentration by 90% at 1200 °C. The dominance of PAHs in tar increased at high thermal cracking temperatures. Zeng et al. [21] analyzed the thermal tar removal in a newly proposed fluidized bed two-stage reaction apparatus. Increased temperature and residence time enhanced the thermal removal of coal pyrolysis tar and eventually the formation of combustible gases. Thermal tar removal efficiencies of 53.8, 62, and 72% were achieved at 950, 1000, and 1050 °C, respectively. Inserted inert Al_2O_3 layer in tar reforming reactor at second stage of the apparatus showed generated coke on its surface.

Different bed materials in tar thermal cracking reactors were tested for the possible complete conversion of tar to combustible gases without coke generation [22,23]. Hosokai et al. [24] investigated the conversion of biomass pyrolysis tar in mesoporous Al_2O_3 and silica sand fixed bed reactors under thermal cracking and steam reforming conditions. Both beds reduced the tar to an undetectable level except benzene and naphthalene. However, higher coke deposition of 45% on Al_2O_3 than 3% of inlet biomass carbon on silica sand was attributed to its highly mesoporous structure and acidic nature. Shimizu et al. [22] observed the coke deposit over Al_2O_3 during conversion of pyrolysis tar. Zeng et al. [21] also observed the coke deposit over Al_2O_3 during thermal conversion of coal pyrolysis tar.

The above stated experimental setups for biomass tar conversion at high temperatures experienced the typical PAHs/coke generation. Use of porous material bed exhibited major operational challenges such as low tar concentration handling and specific bed mass to tar ratio to avoid excessive coke deposit that could deactivate the acidic effect of bed and clog it. Moreover, lighter tar components especially benzene and naphthalene remained unconverted. It is therefore necessary to configure a packed bed reactor assembly guiding the tar conversion to combustible gases instead of coke. This study investigates the conversion of the tar model component benzene in a highly non-porous $\gamma\text{-Al}_2\text{O}_3$ packed bed reactor using steam and CO_2 as reforming media at high temperatures (1000–1100 °C). Selection of such high temperatures is due to having the conditions with probable high in situ coke generation and thus critically analyzing the ability of proposed $\gamma\text{-Al}_2\text{O}_3$ packed bed reactor for desired coke avoided benzene conversion. According authors best knowledge, no study has reported the conversion of tar using a packed bed of this material. This material is highly non-reactive and stable at high temperatures. Material highly non-porous characteristic reduces the probability of deposition of released biomass inherited alkali metals and any escaped char fine particles in case of using real producer gas that may catalyze the tar conversion process. Moreover, it may

eliminate the in situ coke generating reactions inside the pores, continuous progression of which may clog the bed [25]. Therefore, using this material would be able to investigate the steady benzene conversion greatly under thermal reforming conditions. Using benzene instead of real producer/pyrolysis gas may eliminate the possible catalytic effect of alkali metals containing char deposit as mentioned above. Benzene being one of the most difficult convertible tar components as reported in various studies would enable to critically assess a tar conversion technique [24,26]. Moreover, using benzene, a simple and primary tar component, would enable fundamental investigation of its conversion. It may be relatively easy to investigate its mode of conversion either to smaller compounds (e.g., CO , H_2 , CO_2 , CH_4 , C_2H_2) through cracking or higher aromatics (e.g., naphthalene, phenanthrene, anthracene) through polymerization. The influences of packed bed presence, reforming medium (steam and CO_2), concentration of benzene, and gas flow rate on benzene conversion are examined.

2. Materials and methodology

2.1. Materials

Gases (i.e., N_2 and CO_2) with a purity level of 99% (Air Liquide AB, Malmö, Sweden) were used. Benzene with a purity level of 99.7% (Merck, Kenilworth, NJ, USA) was selected as a tar model component due to its excellent thermal stability as mentioned above and high concentration in producer gas from biomass gasifiers. Particles of $\gamma\text{-Al}_2\text{O}_3$ (T-162; Almatix GmbH, Ludwigshafen, Germany) with an average size, mean pore diameter and bulk density of 3 μm , 0.71 μm and 3.60 g/ cm^3 respectively, were used as a packed bed.

2.2. Experimental setup

The reactor assembly used in this study comprises three main sections, i.e., a gas-feeding section, a reactor with a packed bed of Al_2O_3 particles, and a gas analysis section, as shown in Fig. 1. In the gas-feeding section, the supplies of CO_2 and N_2 (a carrier gas for both steam and benzene) were controlled using mass flow controllers (MFCs) (Bronkhorst High-Tech, Ruurlo, Netherlands). Benzene was supplied using a microinjection pump (CMA/100; Stockholm, Sweden) through a concentration stabilizer. A controlled evaporation and mixing (CEM) unit was used to generate steam. The steam concentration was regulated by managing the flow rate of water using a liquid mass flow controller (LMFC) (Bronkhorst High-Tech). To prevent steam condensation, the gas feeding section was heated to 130 °C using heat tapes.

A vertical tubular ceramic reactor (Pythagoras tube; Morgan Advanced Materials, Windsor, UK) with an inside diameter of 27 mm was used for the benzene-conversion experiments. A $\gamma\text{-Al}_2\text{O}_3$ packed bed with a height of 25 cm was installed inside the ceramic reactor. An electrically heated tube furnace (Entech Energiteknik AB, Ängelholm, Sweden) was used to heat the packed bed reactor to the desired temperatures. The temperature profile of reactor was established using a K-type thermocouple.

Reactor outlet gas was analyzed in the gas analysis section. To ensure clean contaminant-free outlet gas for the gas analysis equipment, a high-temperature (HT) thimble filter was installed downstream from the reactor to capture any in situ generated coke or ash particles. Like the

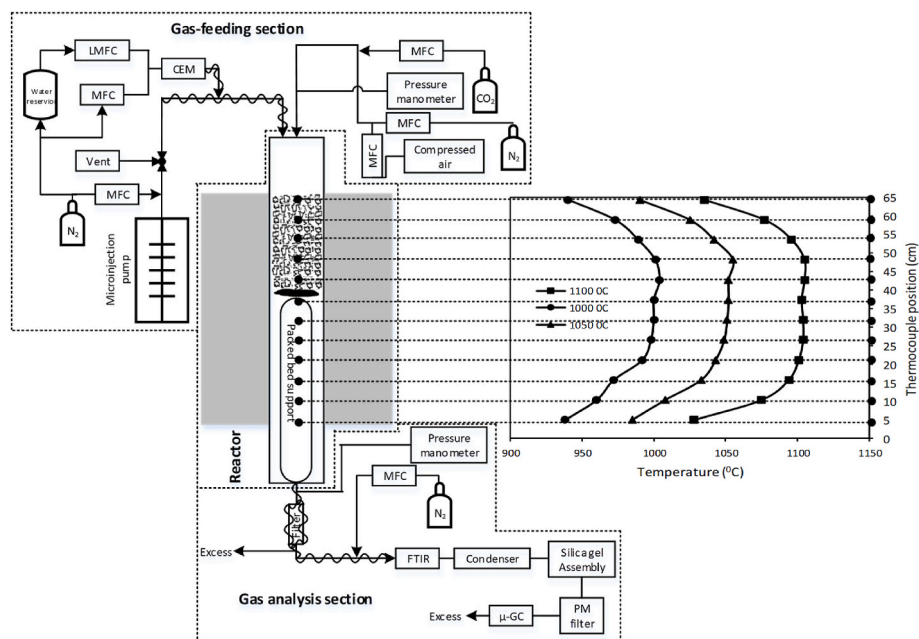


Fig. 1. Experimental setup.

Table 1
Experimental conditions.

Parameter	Influence of packed bed		Influence of reforming medium		Influence of concentrations of reforming medium and benzene			Influence of gas flow rate		
	Packed bed	Without packed bed	Steam reforming	CO ₂ reforming	Effect of steam concentration	Effect of CO ₂ concentration	Effect of Benzene concentration			
Benzene concentration (vol %)	1.4	1.4	1.7	1.7	1.7	1.7	0.45, 1.4, 1.7	1.7	1.1	0.7
Steam concentration (vol%)	24	24	24	–	8, 16, 24	24	24	24	16	10
CO ₂ concentration (vol%)	17	17	–	17	17	6, 12, 17	17	17	11.8	7.3
Gas flow rate (slpm)	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	1.25	2
S/B ^a	4.2	4.2	4.2	–	2.2, 2.4, 3.6	3.6	13.5, 4.1, 3.6	3.6	3.6	3.6
Reactor temperature (°C)	1000, 1050, 1100	1000	1000, 1050, 1100	1000, 1050, 1100	1000	1000	1050	1000	1000	1000
Gas residence time (s)	1.86 ^b , 1.79 ^c , 1.72 ^d	–	1.86, 1.79, 1.72	1.86, 1.79, 1.72	1.86	1.86	1.86	1.86	1.27	0.79

^a Steam to benzene molar ratio.

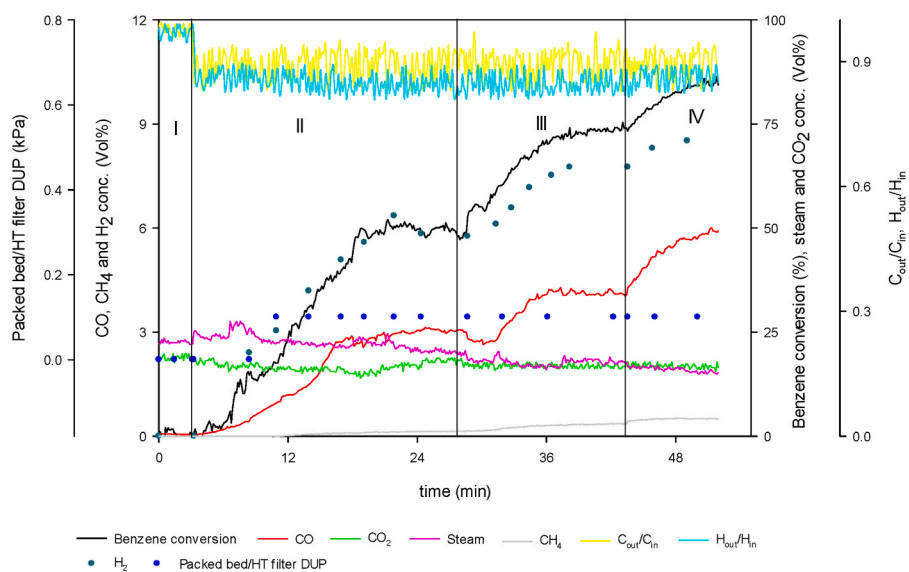
^b at 1000 °C.

^c at 1050 °C and.

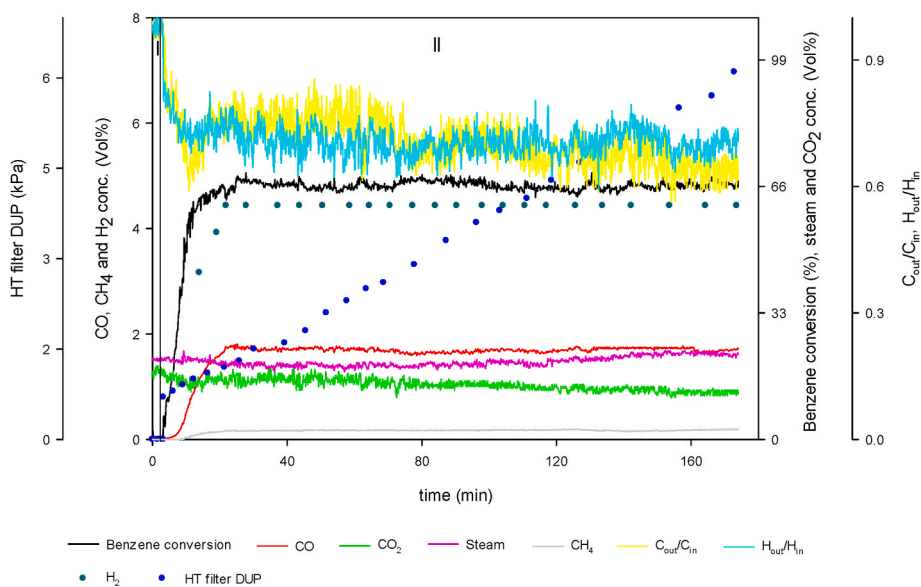
^d at 1100 °C.

assembly upstream from the reactor in the gas-feeding section, the assembly downstream from the reactor was kept heated at 250 °C to prevent steam condensation and the adsorption of benzene and any in situ generated high molecular weight compounds on the HT filter. A Fourier transform infrared (FTIR) gas spectrometer (type DX-4000; Gasmet Technologies Oy, Helsinki, Finland) was used to measure CO, CO₂, CH₄, steam, and benzene concentrations in the reactor outlet gas.

To adjust the concentrations of gas components to be within the measuring range of the FTIR, the entering gas was diluted with N₂; those concentrations of gas components were corrected. The gas exiting the FTIR was led to a cold trap and silica gel assembly before being directed to micro gas chromatograph (model CP-4900; Varian Inc., Palo Alto, CA, USA) for H₂ concentration measurement. The upstream pressures at both the packed bed and the HT filter were measured using pressure



(a)



(b)

Fig. 2. Benzene conversion, concentrations of reactor outlet gases, carbon/hydrogen balances and HT filter DUP (a) during a rise in packed bed reactor temperature from 300 °C in I to 1000 °C in II, 1050 °C in III and 1100 °C in IV (b) during a temperature rise of a reactor without the packed bed from 300 °C in I to 1000 °C in II.

meters (Type PTM 100; Elcanic, Gørtlervej, Denmark).

2.3. Experimental procedure

Experiments for determining the benzene conversion were initiated by heating the reactor to 300 °C under N₂ supply. After the stable reactor temperature was reached, the N₂ supply was replaced with N₂ carrying benzene and steam, CO₂, or a combination of steam and CO₂ as the reforming medium. After stable concentrations of the gas components had been reached, and taking them as the reference conditions for benzene conversion, the reactor temperature was raised to the desired temperature for benzene conversion. After the desired temperature had been reached, the experimental run lasted until stable concentrations of outlet gases (e.g., CO, CO₂, CH₄, H₂, steam, and benzene) were achieved. It occurred after the steady states had been reached in a number of likely reactions, such as benzene and generated methane reforming (e.g., steam and dry reforming), the water–gas shift (WGS) reaction, and the steam/CO₂ gasification of possible in situ generated coke deposit. The producer gas downstream from the reactor was continuously analyzed, which may facilitate to track the possible conversion path of benzene. Temperature profiles of reactor established at different desired temperatures are shown in Fig. 1. The differential upstream pressure (DUP) of either the bed or HT filter, defined as the difference between their upstream pressures at a certain time during the experimental run and at reference condition of benzene conversion, was treated as an indicator of in situ generated coke. Before initiating the next experiment, the reactor was cleaned of any hydrocarbon/coke deposit traces retained from the previous experiment through gasification/combustion using a mixture of steam and excess air. Each experiment performed in this study was repeated twice to confirm the replicability and determine the standard deviation. The detailed experimental conditions are given in Table 1.

Under steady reaction conditions, the N₂ balance is used to determine the reactor outlet gas flow rate:

$$Q_{in} \cdot y_{N_2,in} = Q_{out} \cdot y_{N_2,out} \quad (1)$$

where Q (with subscripts “in” and “out” describing the inlet gas flow rate and outlet gas flow rate, respectively); likewise, $y_{N_2,in}$ (vol%) and $y_{N_2,out}$ (vol%) are the nitrogen concentrations in inlet gas and outlet gas, respectively. $y_{N_2,out}$ was computed through subtraction the summation of measured concentrations of other outlet gas components (e.g., CO, CO₂, CH₄, H₂, C₆H₆, steam).

The benzene conversion at steady state, due to its reforming in the presence of steam, CO₂, or a combination of both at high reactor temperatures, can be calculated as:

$$X = \left[\frac{y_{C_6H_6,in} - y_{C_6H_6,out}}{y_{C_6H_6,in}} \right] * 100 \quad (2)$$

where X represents the benzene conversion.

The yield of produced gases (H₂, CO, CH₄) due to benzene conversion can be computed as its percentage of stoichiometric molar flow rate from reforming reactions given by Eqs. (5) and (6)

$$Y_{H_2} = \frac{y_{H_2,out} \cdot Q_{out} / V_M}{(9/2) \left[(y_{C_6H_6,in} \cdot Q_{in} - y_{C_6H_6,out} \cdot Q_{out}) / V_M \right]} \quad (3)$$

$$Y_i = \frac{y_{i,out} \cdot Q_{out} / V_M}{9 \left[(y_{C_6H_6,in} \cdot Q_{in} - y_{C_6H_6,out} \cdot Q_{out}) / V_M \right]} \quad (4)$$



Where Y represents the yield and i in Eq. (4) represents CO or CH₄. Due to various reactions involved in benzene reforming process, similar stoichiometric ratio is assumed for CH₄ as with CO. While, V_M (L/mol) is the molar volume of an ideal gas at normal temperature and pressure (i. e., 20 °C and 1 bar). The carbon and hydrogen mass balances, indicators of coke generation, can be computed using the expressions:

$$\text{Carbon balance} = \frac{C_{out}}{C_{in}} \quad (7)$$

$$\text{Hydrogen balance} = \frac{H_{out}}{H_{in}} \quad (8)$$

where C_{in} (g/min) = $\frac{Q_{in} \cdot M_C \cdot (y_{CO_2,in} + y_{C_6H_6,in})}{V_M}$ and C_{out} (g/min) = $\frac{Q_{out} \cdot M_C \cdot (y_{CO,out} + y_{CO_2,out} + y_{CH_4,out} + y_{C_6H_6,out})}{V_M}$, M_C (g/mol) is the molar mass of carbon. Similarly, H_{in} (g/min) = $\frac{Q_{in} \cdot M_H \cdot (2 \cdot y_{steam,in} + 6 \cdot y_{C_6H_6,in})}{V_M}$ and H_{out} (g/min) = $\frac{Q_{out} \cdot M_H \cdot (2 \cdot y_{steam,out} + 2 \cdot y_{H_2,out} + 4 \cdot y_{CH_4,out} + 6 \cdot y_{C_6H_6,out})}{V_M}$, M_H (g/mol) is the molar mass of hydrogen.

Coke deposit determination: A combustion approach was used to estimate the coke deposit, m_{coke} (g). It began by diverting the inlet benzene flow towards the vent at the end of an experiment while simultaneously stopping the flow of reforming medium and maintaining the N₂ flow. A little air was supplied to partially combust the coke deposit. The reactor outlet gas was analyzed using downstream gas analysis equipment. The combustion was continued until the concentrations of carbon-containing gases (e.g., CO, CO₂, and CH₄) dropped to insignificant levels; m_{coke} was established as the total carbon released in the form of CO, CO₂, and CH₄ during combustion. It was calculated using the following equation:

$$m_{coke} = \sum_0^{t_g} \frac{[y_{CO}(t) + y_{CO_2}(t) + y_{CH_4}(t)] * Q_{out} * \Delta t * M_C}{V_m} \quad (9)$$

where y_{CO} , y_{CO_2} , and y_{CH_4} are the concentrations of CO, CO₂, and CH₄, respectively, in the reactor outlet gas; t_g is the total duration for partial combustion of coke deposit and Δt (min) is the time interval between two data points.

3. Results and discussion

3.1. Influence of temperature and presence of packed bed

Fig. 2 (a) shows the benzene conversion and concentrations of reactor outlet gases during an increase in temperature of packed bed reactor from 300 to 1100 °C. The increased concentrations of combustible gases with increase in benzene conversion at increasing temperatures are evident. Steady states approached after attaining steady concentrations of outlet gases are visible in regions II, III and IV. Steady state benzene conversions of 52, 75, and 84% were achieved at 1000,

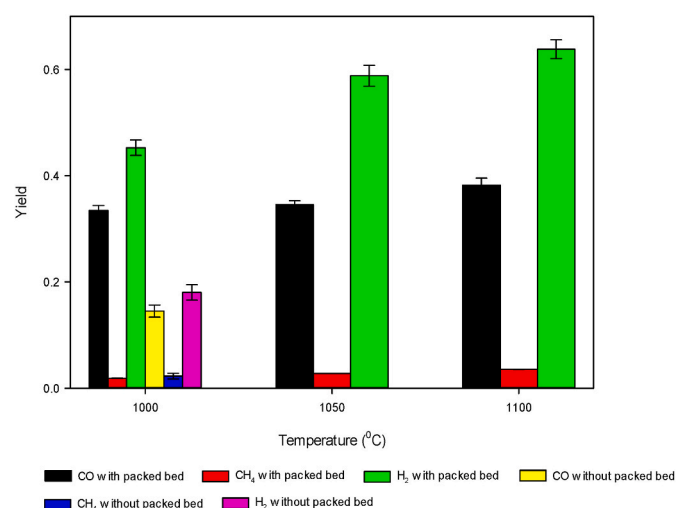


Fig. 3. Yields of gases produced from steam + CO₂ reforming of benzene with and without a packed bed at different temperatures.

1050, and 1100 °C, respectively. Corresponding carbon and hydrogen balances of 0.86–0.90 and 0.84–0.87 respectively showed their negligible losses. Moreover, the experiment was reproducible within the computed standard deviations of 0.7–1.5% for benzene conversion and of 0.1–0.6% (CO), 0.3–0.75% (CO₂), 0.02–0.06% (CH₄), 0.6–1% (H₂), and 0.7–1.2% (steam) for concentrations of gases. The gradual decrease in reforming medium concentration with increasing temperature is also obvious. The packed bed/HT filter DUP did not fluctuate and remained stable during the experimental run indicating no generation of in situ coke. Apart from that, visual inspection of both packed bed reactor and HT filter after experiment completion and the cooling of the experimental setup to room temperature under N₂ supply indicated no traces of coke. However, γ -Al₂O₃ particles were covered with a steady thin sticky layer of coke. Similar but rather loose form of coke deposit over porous γ -Al₂O₃ bed particles was observed during steam reforming of biomass pyrolysis tar [24].

Fig. 2 (b) shows the benzene conversion and concentrations of reactor outlet gases during a temperature increase of reactor without a packed bed from 300 to 1000 °C. Without the packed bed, it established nearly homogeneous reforming of benzene by neglecting the effect of reactor walls. With an increase in temperature, the rise in benzene conversion and concentrations of combustible gases are obvious in region II. A steady state benzene conversion of 65% was achieved at a reactor temperature of 1000 °C. The experiment was repeatable within the computed standard deviation of 2% for benzene conversion and of 0.8% (CO), 0.95% (CO₂), 0.08% (CH₄), 1.3% (H₂), and 1.5% (steam) for concentrations of gases. Steady state reached after attaining the stable concentrations of reactor outlet gases, whereas, a gradual rise in HT filter DUP was observed. To elaborate it and its effects on process (e.g., benzene conversion, concentrations of gases) further, the experiment was continued bit longer. A linear similar gradual increase in HT filter DUP with stable benzene conversion and concentrations of outlet gases except the reforming media was observed. It could be due to deposition of in situ generated coke inside the HT filter. Moreover, the visual

inspection of both reactor and HT filter after experiment completion revealed thick layers of coke adhering to walls. The high carbon and hydrogen losses with carbon and hydrogen balances of 0.62–0.67 and 0.68–0.75 were in line as well. Comparing the benzene conversions and corresponding carbon balances with and without the packed bed indicated that insertion of packed bed surface in the reactor reduced the benzene conversion. Whereas, the presence of packed bed with possible surface reactions prevented the conversion of benzene to coke compared to case without the packed bed and thus resulted into low carbon and hydrogen losses than without the packed bed. Relative high benzene conversion due to homogeneous reforming without the packed bed than with the packed bed could be due to in situ generated coke. Similar finding of coke generation was observed during homogeneous thermal cracking of producer gas tar at high temperatures (900–1075 °C) [27]. Achieved relative high concentrations of 2.3 vol% and 6 vol% than 1.4 vol% and 4.7 vol% of CO and H₂ with and without the packed bed respectively, may indicate the packed bed ability to convert the benzene to combustible gases. Comparing the yields of these produced gases presented in Fig. 3 may better reveal the effect of packed bed. High CO and H₂ yields of 0.33 and 0.47 with packed bed than 0.16 and 0.20 without the packed bed respectively even with comparatively low benzene conversion and carbon loss reveal benzene decomposition to combustible gases instead of coke.

3.2. Influence of temperature and reforming medium

The effects of steam and CO₂ reforming on benzene conversion and concentrations of reactor outlet gases at different temperatures of packed bed reactor are shown in Fig. 4. Since the procedures and analytical approaches for all presented experiments are similar, Fig. 4 shows only the steady state values of different responses with error bars indicating their standard deviations. However, the detailed experimental data for this and ahead sections has been presented as supplementary material. Steam reforming of benzene at increased reactor temperatures increased both the benzene conversion and the concentrations of combustible gases as shown in Fig. 4 (a). Reactor temperatures of 1000, 1050, and 1100 °C achieved steady state benzene conversions of 42, 65, and 80%, respectively. The corresponding carbon and hydrogen balances of 0.85–0.91 and 0.86–0.89 respectively showed their little losses. The packed bed/HT filter DUP remained stable near zero at selected temperature range and experimental duration.

CO₂ reforming achieved relative higher benzene conversions than with steam reforming under similar experimental conditions as apparent from Fig. 4 (b). Steady state benzene conversions of 68, 90, and 98% were achieved at reactor temperatures of 1000, 1050, and 1100 °C, respectively. Carbon and hydrogen balances of 0.85–0.89 and 0.87–0.90 respectively were attained. Higher benzene conversions with CO₂ reforming than with steam reforming indicated higher reactivity of CO₂ than steam for benzene cracking. Higher CO concentrations than achieved with steam reforming at different reactor temperatures could be attributed to Boudouard reaction in presence of coke deposit. Lower H₂ concentrations than achieved with steam reforming at different reactor temperatures are also evident. Comparing the CO and H₂ yields achieved with steam and CO₂ reforming presented in Fig. 5 showed similar trend; high CO yield of 0.47–0.66 with CO₂ reforming than of 0.33–0.38 achieved with steam reforming and low H₂ yield of 0.17–0.19 than of

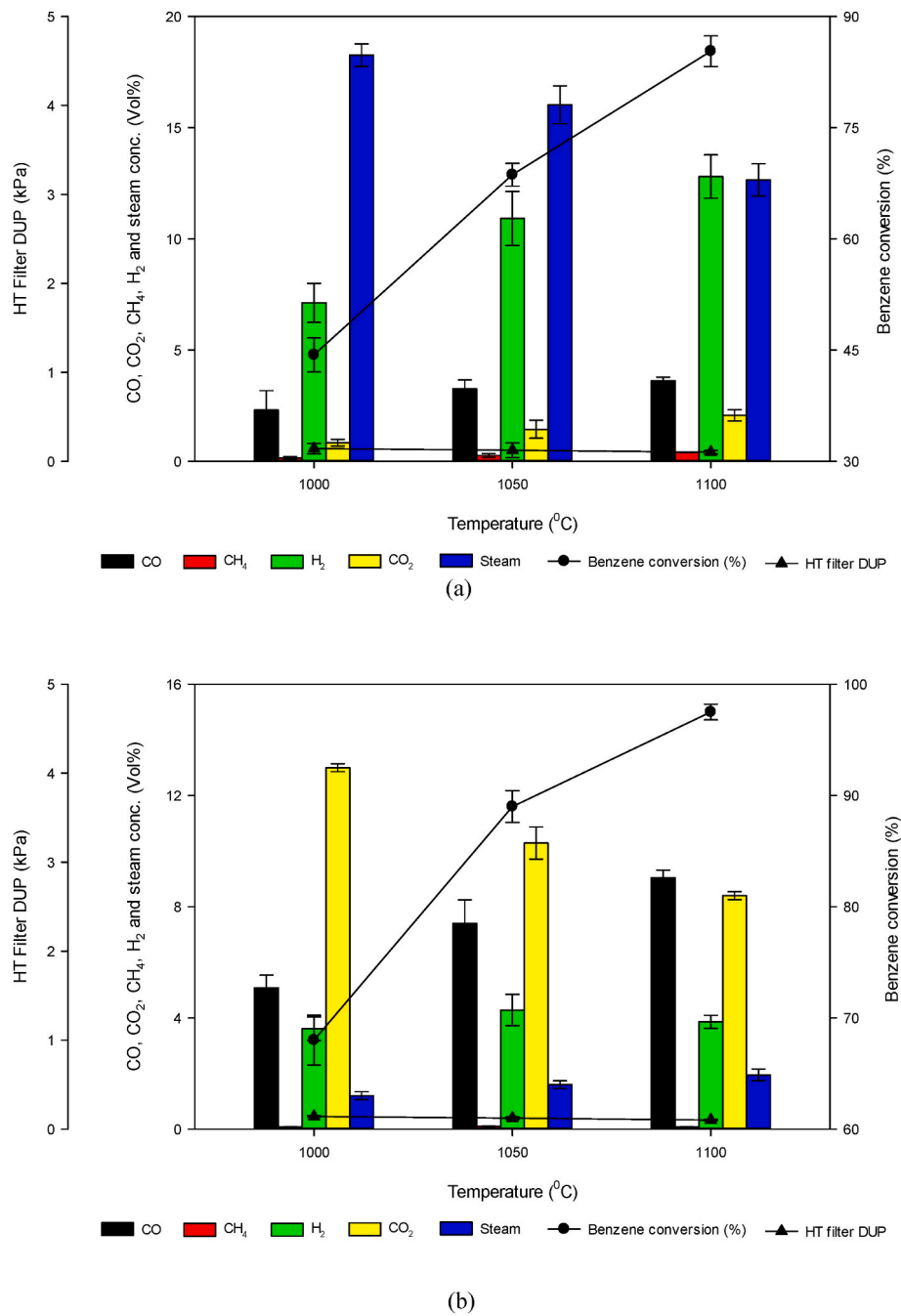


Fig. 4. Steady state benzene conversions, concentrations of reactor outlet gases, and HT filter DUP at different packed bed reactor temperatures using (a) steam and (b) CO₂ as a benzene reforming media.

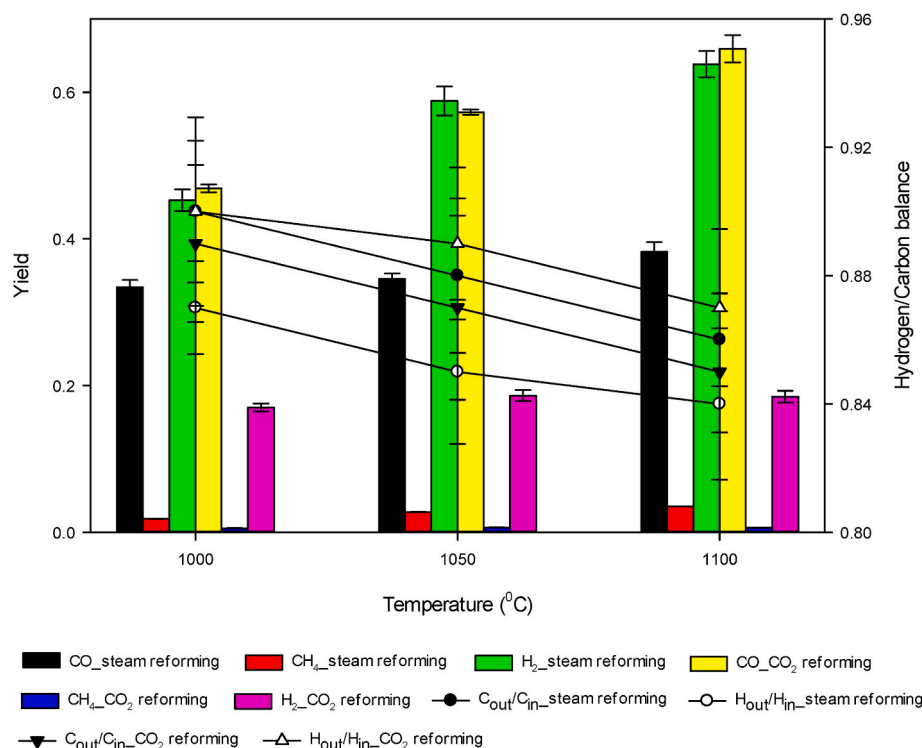


Fig. 5. Hydrogen/carbon balances and yields of gases produced from steam and CO₂ reforming of benzene at different temperatures of packed bed reactor.

0.45–0.63 achieved with steam reforming. The Packed bed/HT filter DUPs of around zero at all investigated temperatures are noticeable in the figure.

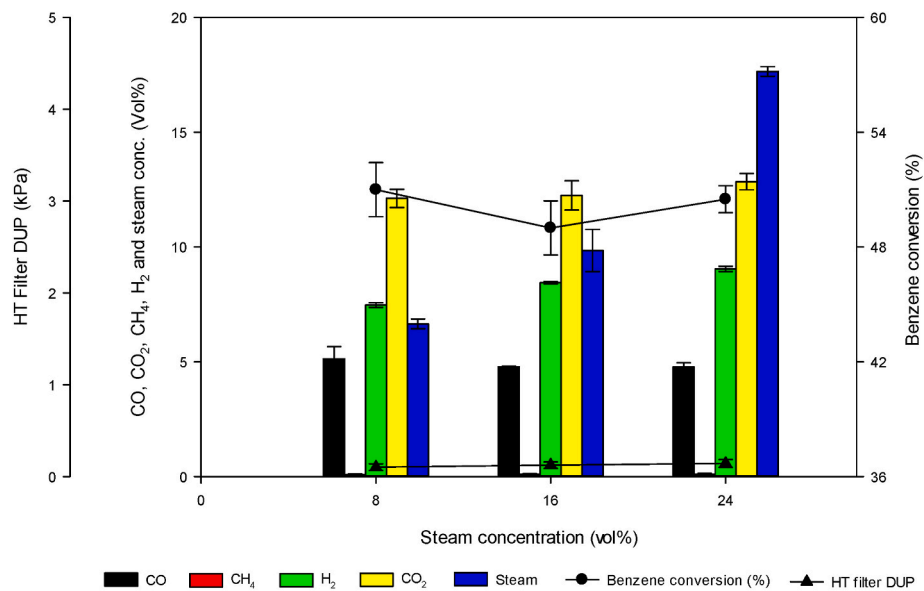
3.3. Influence of concentrations of reforming medium and benzene

Fig. 6 shows the benzene conversions and concentrations of reactor outlet gases at different concentrations of steam and CO₂, and 1000 °C. Different tested steam concentrations (i.e., 24, 16, and 8 vol%) achieved nearly similar benzene conversions of approximately 52%. Computed corresponding carbon and hydrogen balances of 0.84–0.90 and 0.85–0.88 respectively showed their negligible losses. Nearly similar CO concentrations were achieved at different tested steam concentrations. Increasing H₂ concentrations with increasing steam concentrations are also obvious from Fig. 6 (a). Stable packed bed/HT filter DUPs near zero at different tested steam concentrations are visible.

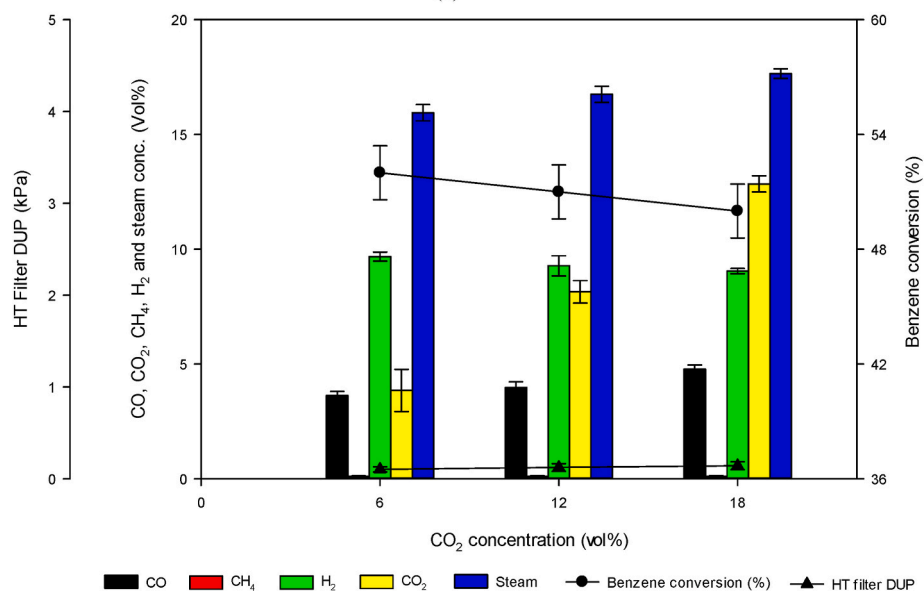
Different CO₂ concentrations (i.e., 6, 12, and 17 vol%) achieved nearly similar benzene conversions of approximately 52% as achieved with different steam concentrations as visible in Fig. 6 (b). Corresponding carbon and hydrogen balances were 0.85–0.90 and 0.88–0.90 respectively. Slightly increasing and decreasing concentrations of CO and H₂, respectively, with increasing CO₂ concentrations were observed and could be attributable to a reduced WGS reaction. Computed CO and H₂ yields as presented in Fig. 7 were in line with their respective achieved concentrations; nearly similar and increasing CO and H₂ yields with increasing steam concentration, and contradictory increasing and

decreasing CO and H₂ yields with increasing CO₂ concentration. Stable packed bed/HT filter DUPs near zero at different CO₂ concentrations are evident. Equivalent benzene conversions with both steam and CO₂ reforming at their different concentrations could be attributed to prevailing excess conditions, i.e., greater amounts of reforming media than stoichiometric amounts. Swierczynski et al. observed similar toluene conversions over Ni/olivine catalyst at steam/toluene of 7.5–24 [28]. It also implies that any additional formation of reforming media during benzene reforming may not have influence on benzene conversion. In addition, produced gases with varying concentrations at different concentrations of reforming media also showed no particular influence on benzene conversion. Such negligible effects of CO, CH₄ and H₂ on tar model conversion have been reported in literature [29,30].

The influence of an increase in benzene concentration on the benzene conversion itself during steam + CO₂ reforming and concentrations of reactor outlet gases is shown in Fig. 8. Increase in benzene concentration from 0.45 to 1.7 vol% decreased the benzene conversion from 75 to 62% while the concentrations of combustible gases increased. Corresponding carbon and hydrogen balances of 0.87–0.92 and 0.85–0.91 respectively, were estimated. However, steady state conditions were attained bit later during changing the benzene concentration than changing other parameters (e.g., steam/CO₂ concentration, temperature) in above sections. Earlier achieved steady state conditions during changing the steam concentration (24–16 vol%) than changing the benzene concentration (0.45–1.7 vol%) is visible from Fig. S2 (a) and S2 (c). It may be attributed to appreciable newly established coke deposit.



(a)



(b)

Fig. 6. Steady state benzene conversions, concentrations of reactor outlet gases, carbon percentage error, and HT filter DUP at different (a) steam and (b) CO₂ concentrations at a packed bed reactor temperature of 1000 °C.

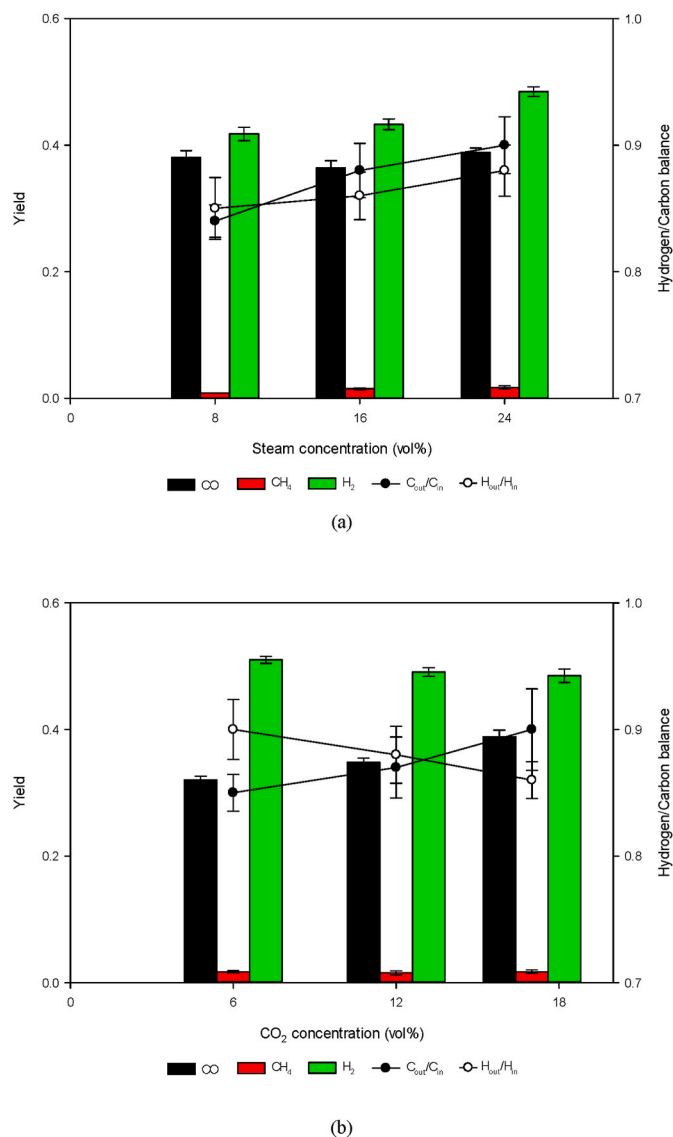


Fig. 7. Hydrogen/carbon balances and yields of gases produced from benzene reforming at different concentrations of (a) steam and (b) CO₂ at a packed bed reactor temperature of 1000 °C.

Increasing and decreasing concentrations of H₂ and reforming media respectively with increasing benzene concentration are evident. Computed CO and H₂ yields presented in Fig. 9 also showed their increasing trend with increase in benzene concentration. Stable packed bed/HT filter DUP close to zero at investigated benzene concentrations is apparent.

3.4. Influence of gas flow rate

Fig. 10 shows the benzene conversions and concentrations of reactor

outlet gases at different gas flow rates and 1000 °C. Increase in gas flow rate from 0.85 to 2 slpm decreased the benzene conversion from 52 to 18%. It could be attributed to reduced gas residence time with increasing gas flow rate that had significant effect on benzene conversion. Corresponding carbon and mass balances of 0.86–0.91 and 0.85–0.90 respectively, were estimated. Stable packed bed/HT filter DUP near zero at different gas flow rates is visible in Fig. 10. Computed yields of gas products shown in Fig. 11 are in line with respective concentrations that decrease with an increase in gas flow rate.

3.5. Coke deposit measurement

The steady state masses of coke deposits, m_{coke} (g), on the bed particles in above-described benzene reforming experiments are depicted in Fig. 12. Measured m_{coke} were 3–5, 10–15 and 8–12% of inlet carbon for combined steam and CO₂ reforming, steam reforming and CO₂ reforming respectively. These coke deposits with high tar/benzene concentration of 45% of inlet carbon with low tar concentration of 0.8 vol% [24]. It indicated the ability of this novel packed bed reactor to convert high concentrations of tar without causing bed blockage due to excessive in situ generated coke deposit. In steam reforming, the mass of the coke deposit decreased with increasing temperature, whereas it increased both in combined steam and CO₂ reforming and CO₂ reforming. However, higher coke deposits in CO₂ reforming than in steam reforming at the tested temperatures may be due to lower gasification reactivity of CO₂ relative to steam. Similar relatively high reaction rates of coke/char gasification with steam than with CO₂ have been reported in literature [31,32]. It may be attributed to difference in intrinsic reaction rates of steam and CO₂ gasification occurring at similar active sites of coke [33, 34]. Whereas, low coke deposits in combined steam and CO₂ reforming than both in steam reforming and CO₂ reforming at 1000 and 1050 °C may be attributed to their cumulative gasification/synergistic effect. Such synergistic effect for combined steam and CO₂ of char have been reported in literature [33,35].

4. Benzene conversion kinetics

Benzene conversion in a packed bed reactor could be simplified to a first order reaction provided plug flow conditions and no effect of reforming media (high excess) on benzene conversion are assumed. First order kinetic equation can be given as

$$\frac{dC_6H_6}{d\tau} = kC_6H_6 \quad (10)$$

The apparent reaction rate constant k (m³ kg⁻¹ h⁻¹) was obtained from following Eq. (11) and reported in Table 2. Weight time, τ (kg m⁻³ h) defined as ratio of packed bed weight to gas flow rate is used instead of just residence time as both packed bed and residence time contribute to benzene conversion.

$$k = \frac{-\ln(1 - X)}{\tau} \quad (11)$$

k appears a suitable parameter to compare tar conversions achieved at different experimental conditions as widely reported in literature [9, 36,37]. Rearranging Eq. (11) for X gives

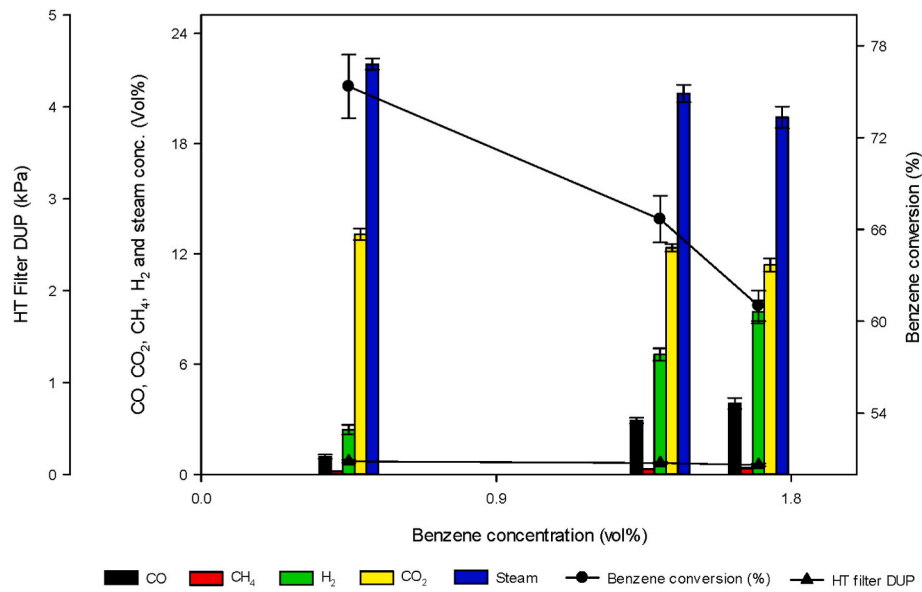


Fig. 8. Steady state benzene conversions, concentrations of reactor outlet gases, carbon percentage error, and HT filter DUP during steam + CO₂ reforming of benzene at different benzene concentrations and a packed bed reactor temperature of 1050 °C.

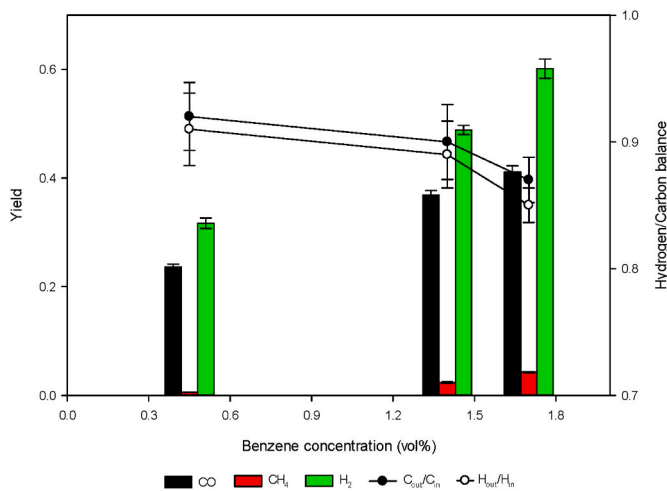


Fig. 9. Hydrogen/carbon balances and yields of gases produced from steam + CO₂ reforming of benzene at its different concentrations and packed bed reactor temperature of 1050 °C.

$$X = (1 - \exp(-k\tau)) \times 100 \quad (12)$$

Eq. (12) presents a general established model to estimate the benzene conversions at different experimental conditions (reactor temperature in present study). This model was fitted to experimentally determined benzene conversions achieved using different reforming media at 1000–1100 °C. Fig. 13 shows the model computed benzene conversion plots at different temperatures and as a function of τ . The trend of plot at 1000 °C indicates that benzene conversion of more than 95% would be achieved at τ exceeding 9 kg m⁻³ h. Similar with plots at 1050 and 1100 °C; benzene conversions of 95% at τ values of 4.15 and 2.8 kg m⁻³ h respectively.

5. Conclusion

Conversion of tar model benzene in a novel highly non-porous γ -Al₂O₃ packed bed reactor was investigated at 1000–1100 °C. The influences of presence of packed bed, reforming medium (steam and CO₂), gas flow rate and benzene concentration on steady state benzene

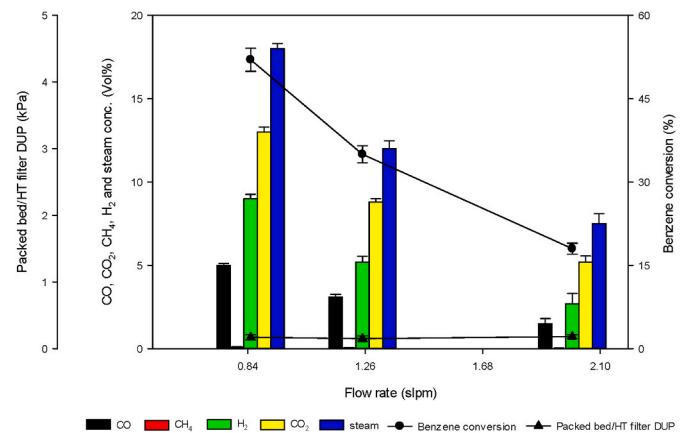


Fig. 10. Steady state benzene conversions, concentrations of reactor outlet gases and HT filter DUP during steam + CO₂ reforming of benzene at different gas flow rates and a packed bed reactor temperature of 1000 °C.

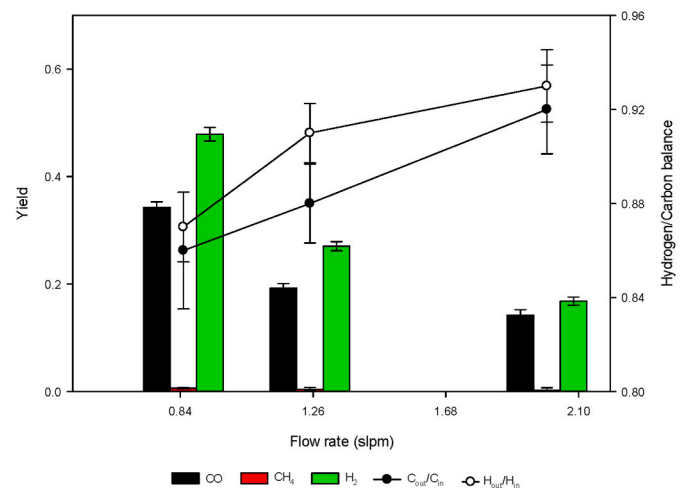


Fig. 11. Hydrogen/carbon balances and yields of gases produced from benzene reforming at different gas flow rates and packed bed reactor temperature of 1000 °C.

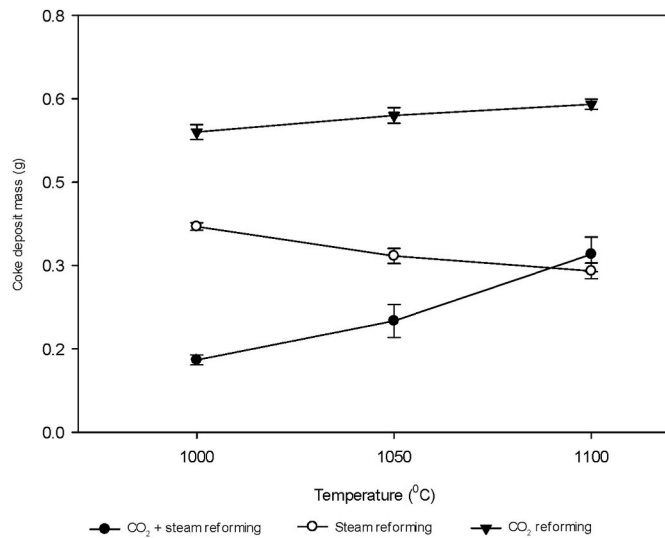


Fig. 12. Mass of steady state coke deposits during benzene conversion using different reforming media at different temperatures.

Table 2

Estimated values of k for first order kinetic assumed benzene conversion with different reforming media at 1000–1100 °C.

Temperature (°C)	1000	1050	1100
k (m ³ kg ⁻¹ h ⁻¹)	0.33	0.73	1.07

conversion were examined. Packed bed reactor achieved benzene conversions of 52, 75 and 84% with combined steam and CO₂ reforming at 1000, 1050 and 1100 °C respectively. Whereas, high benzene conversion of 65% was achieved without the packed bed at 1000 °C, however, a continuous increase in the HT filter DUP due to deposition of in situ generated coke was observed. Relative high concentrations of generated CO and H₂ of 2.3 vol% and 6 vol% with packed bed than 1.4 vol% and 4.7 vol% without the packed bed respectively, were achieved. Concerning the influence of reforming media, CO₂ reforming achieved higher benzene conversions of 68, 90, and 98% than 42, 65, and 80% with steam reforming at packed bed temperatures of 1000, 1050, and 1100 °C, respectively. Varying concentrations of either steam or CO₂ did not influence the benzene conversion. Increasing both gas flow rate and benzene concentration decreased the Benzene conversion. Low steady thin coke deposits observed on bed particles were 3–5, 10–15 and 8–12% of inlet carbon mass for combined steam and CO₂ reforming, steam reforming and CO₂ reforming respectively. The results indicated that presence of packed bed with possible surface reactions converted the benzene into combustible gases compared to the case without the packed bed where benzene was greatly converted to coke.

Additional parametric investigation of packed bed (e.g., height, position, and shape/size of bed particles) in connection with other operating parameters (e.g., reactor temperature, gas residence time, and benzene concentration) would be an interesting future work. It would facilitate in depth evaluation of thermal approach for tar conversion and an opportunity for its improvement.

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.

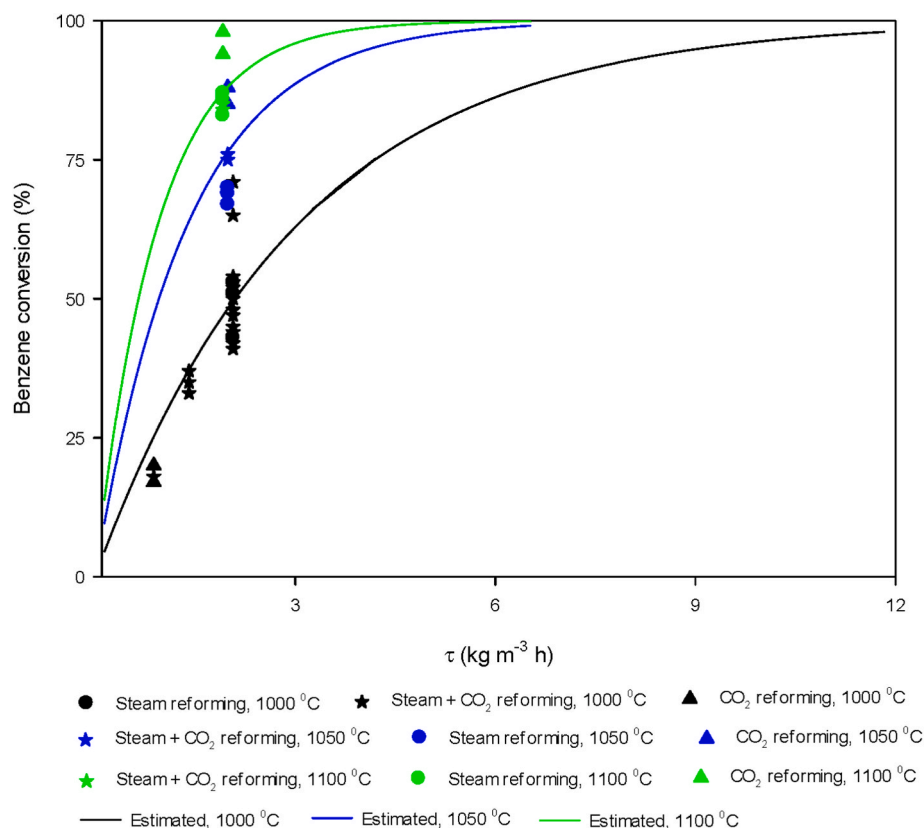


Fig. 13. Benzene conversions as a function of weight time (τ , kg m⁻³ h) at different temperatures and reforming media.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.joei.2023.101307>.

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