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Process improvement analysis of pyrolysis/gasification of biomass and waste plastics with carbon capture and utilisation through process simulation

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ABSTRACT

Excessive utilisation of fossil fuels to meet increasing energy demand results in increasing global CO_2 emissions. It is a promising solution to apply carbon capture and utilisation (CCU) for pyrolysis/gasification of biomass and waste plastics, which recycles captured CO_2 from pyrolysis/gasification to the reforming stage to serve as the second gasification agent. This paper aims to analyse the potential of combining the pyrolysis/gasification process with CCU and to investigate how to improve this process through process simulation using Aspen Plus®. Process analysis is carried out based on the validated model to investigate the impact of recycling captured CO_2 on the product gas production and CO_2 conversion when changing various operating conditions (i.e. the amount of recycled CO_2, reforming temperature and steam-to-feed ratio). The target is to ensure high H_2 production and to promote CO_2 conversion. Simulation results indicated that: (i) Applying CCU for pyrolysis/gasification can inhibit the production of H_2 andCO_2, but it can promote the production of CO; (ii) The H_2/CO ratio of gas products can be adjusted flexibly after recycling CO_2 to the reforming stage; (iii) Increase of CO_2 recycle amount and steam-to-feed ratio results in lower CO_2 conversion while the increase of reforming temperature improves the CO_2 conversion; (iv) It is suggested to add solid carbon (e.g. bio-char or carbon-based catalyst) in the reforming stage together with adjusting the operating conditions (i.e. relatively high reforming temperature (e.g. 600 ~ 700 °C) and low steam-to-feed ratio (e.g. 3 ~ 4)) simultaneously to protect H_2 production and achieve high CO_2 conversion. The findings in this paper will be very useful for future large-scale commercial deployment of applying CCU for pyrolysis/gasification.

1. Introduction

1.1. Background

Fossil fuel is still the main energy source and it is facing continuous depletion when the global energy demand is expected to keep rising by 28% between 2017 and 2040 [35]. With the large consumption of fossil fuels, a huge amount of CO_2 is released into the environment, causing global warming [14]. To change the heavy reliance on traditional fossil fuels, new methods of fuel and energy production are required to be renewable and clean at the same time. Pyrolysis/gasification is a promising technology to achieve these two requirements due to its wide adaptability to various carbon-based feedstocks (e.g. coal, biomass and waste plastics) [8].

Biomass is a kind of renewable feedstock that can realise carbon-neutrality by consuming nearly the same amount of CO_2 during growth compared to the CO_2 released during energy production [17,41]. It has been developed as a worldwide trend to investigate technologies using biomass for energy production with higher efficiency and economic benefit. The European Union determines the target of 32 % renewable energy to account for the total energy supply by 2030 [15]. Biomass provided around two-thirds of primary renewable source production in 2014, which is currently the largest form of renewable energy in the EU. In the future, biomass will remain a key renewable energy source in 2030 and beyond [20].

Plastics is a kind of high molecular weight material with wide use and high production annually [40]. Different types of waste plastics are difficult to be naturally decomposed due to their complicated properties. A huge amount of waste plastics is discarded into the environment every year to impose severe negative influences on land and aquatic creatures

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Table 1
Overview of key previous studies on pyrolysis/gasification of biomass or plastics through modelling and simulation.

Researchers	Model Type	Raw Materials		Reactor Type	Temperature (°C)		Air	Steam
		Biomass	Plastic		Pyrolysis	Gasification		
Nikoo and Mahinpey [29]	Steady State, Hydrodynamic and kinetic model	Pine sawdust	–	Fluidised Bed	–	700–900	0.19–0.27 (ER)	0–4 (S/F)
Kannan et al. [22]	Steady State, Kinetic model	–	PE	Fluidised Bed	800	800	0.05–0.25 (ER)	0.1–0.8 (S/F)
Begum et al. [7]	Steady State, Gibbs Free Energy Minimization	Wood, Green Waste	–	Integrated Fixed Bed	–	500–1000	1–10 (kg/h)	–
Amoodi et al. [3]	Steady State, Gibbs Free Energy Minimization	–	PE	Fluidised Bed	–	500	–	0.05–5 (S/F)
Mohammed et al. [27]	Steady State, Gibbs Free Energy Minimization	Municipal Green Waste	–	Rotary Furnace	500	–	–	–
Rafati et al. [32]	Steady State, Kinetic Model	Wood	–	Fluidised Bed	–	950–1100	0.25–0.45 (ER)	0–1 (S/F)
Pauls et al. [31]	Steady State, Kinetic Model	Pine sawdust	–	Fluidised Bed	–	700–900	0.19–0.27 (ER)	0–3 (S/F)
Deng et al. [13]	Steady State, Gibbs Free Energy Minimization	MSW	–	Up-Draft Fixed Bed	500	550–1000	–	0–1 (S/F)
Kaushal and Tyagi [23]	Steady State, Kinetic model	Wood	–	Fluidised Bed	–	700–820	–	0.5–1 (S/F)

[12]. It is reported that nearly 60 million tonnes of waste plastics are generated each year within Europe but only 27.3 % of waste plastics go through centralised treatment through landfill [5]. The rest of the waste plastics are just discarded without proper treatment. Therefore, it is urgent to find a new approach to treating waste plastics with high efficiency. Converting waste plastics for energy supply is a promising method due to its intensive hydrocarbon structures.

It has been a trend to combine different feedstocks for pyrolysis/gasification technology [34,39]. Co-pyrolysis/gasification of biomass and waste plastics can help to improve the performance of product yields and the flexibility of feedstock due to the synergic effect between the two types of feedstocks [26]. Compared to pyrolysis/gasification of single biomass or plastics, better product distribution with higher gas yield and less char yield can be achieved [9]. In addition, co-pyrolysis/gasification could also help to improve H_2 production because of the higher H element in waste plastics [16].

Although the pyrolysis/gasification process can generate less CO_2 compared to direct combustion, the attempts to decrease the CO_2 emissions to a larger extent never stop [28]. Carbon capture and utilisation (CCU) is a technology that is developed from carbon capture and storage (CCS) technology. CCS is defined as the process that separates CO_2 from industrial and energy-related sources. The captured CO_2 is stored to be isolated from the atmosphere for a long term, thus alleviating the CO_2 emissions [38]. Compared to CCS, CCU is to use the captured CO_2 for specific new use rather than leaving CO_2 no use for storage. To link CCU technology with pyrolysis/gasification process, the CO_2 generated from pyrolysis/gasification process is captured and then recycled to the reforming stage to serve as the second gasification agent. This will improve the product distribution and further decrease the CO_2 emission.

During pyrolysis/gasification, carbon-based materials such as biochar or activated carbon have the advantages of relatively high catalytic activity and good pore structure [9]. These carbon materials can be directly used for reactions. In addition, they can be used as catalyst support [6,42]. The use of these carbon-based materials or relevant catalysts can help to promote gas production and optimiseproduct distribution [33]. In addition, the existence of carbon-based materials has the potential to increase the CO_2 conversion through Boudouard reaction when the captured CO_2 is recycled to pyrolysis/gasification system.

1.2. *Motivation of this study*

The main driver of this study is to investigate the feasibility of applying CCU to pyrolysis/gasification of biomass and waste plastics for preliminary decision making. The proposed technology can help to solve the key global issues of high CO_2 emissions and severe plastic pollution while meeting energy demand simultaneously. However, it should be noted that the development of separate pyrolysis/gasification and CCU technologies are still not mature enough for large scale commercialisation [8]. Therefore, more studies are required to bring innovative breakthroughs. Using simulation software such as Aspen Plus®, complex processes can be investigated and improved.

Another motivation is to find methods to ensure high H_2 production and promote CO_2 conversion of captured CO_2. After applying CCU to pyrolysis/gasification process, CO_2 is recycled to the reforming stage to serve as the second gasification agent. It is predicted that the H_2 production will be restricted due to CO_2 recycling. This is because the water–gas-shift (WGS) reaction may be hindered. H_2 is the main product of pyrolysis/gasification process with high economic benefits, which can bring the majority of profits [11,24]. It is not practical and meaningful if the H_2 production is decreased a lot. In addition, CO_2 is converted to CO through the process and the extent of CO_2 conversion reflects the efficiency of CO_2 utilisation. It is important to improve the conversion of captured CO_2 for further large-scale commercial deployment.

1.3. *Aim of this study*

This study aims to analyse the potential of combining pyrolysis/gasification process with CCU and to investigate how to improve this process. This research is achieved through process modelling and simulation. A steady-state lumpsum model is required to be developed and Aspen Plus® is convenient to simulate the integrated process effectively and accurately. Process analysis is carried out based on the validated model to investigate the influence of recycling captured CO_2 on the gas production and CO_2 conversion when changing various operating conditions (i.e. the amount of recycled CO_2, reforming temperature and steam-to-feed (S/F) ratio). The target is to ensure high H_2 production and to promote CO_2 conversion.

1.4. *Novelty of this study*

The novelty of this study includes:

(1) No previous studies can be found to apply CCU to pyrolysis/gasification neither through experiments nor through simulations. There are many previous papers only focusing on simulation studies of pyrolysis/gasification of biomass or plastics (see

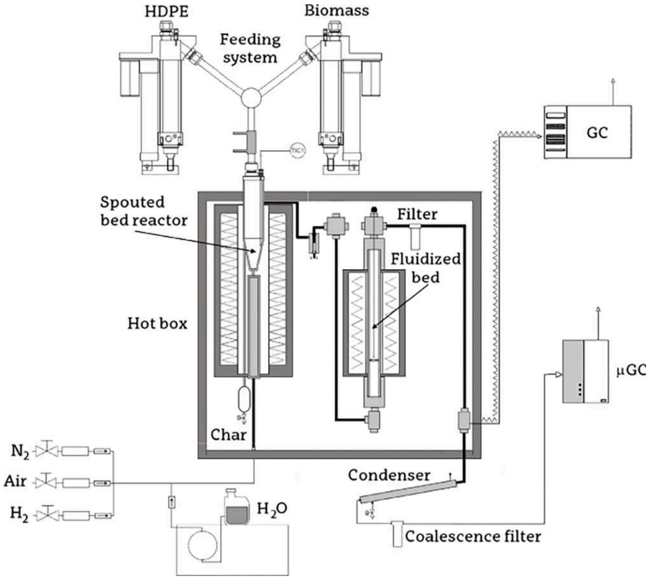

Fig. 1. Process flow diagram for the Pyrolysis - Reforming Experimental rig [4].

Table 1). In this paper, the developed pyrolysis/gasification model was improved to integrate with CCU for investigation.

(2) The performance of applying CCU to pyrolysis/gasification is tested to give a preliminary evaluation of the practical value and feasibility of this technology. Before any technology is applied in real life, a preliminary design evaluation is necessary to test whether it is suitable for further development. In this paper, the possibility to combine CCU and pyrolysis/gasification is demonstrated.

(3) Detailed process analysis was carried out by changing various operating conditions (e.g. recycling CO_2 amount, reforming temperature and S/F ratio) to investigate the influence of recycling captured CO_2 to the pyrolysis/gasification process on the gas production and CO_2 conversion. Key insights about how the integration will influence gas production and CO_2 conversion can be obtained.

(4) In addition, two methods including changing operating conditions and adding solid carbon are put forward to ensure H_2 production and promote CO_2 conversion. Especially for the method of solid carbon addition, extra process analysis was performed by adding a new feed stream to the reforming stage to investigate the influence of carbon addition amount on the CO_2 conversion. These findings will be useful for future large-scale commercial deployment.

2. Model development and validation

2.1. Introduction to the selected experimental rig

In this paper, a two-stage pyrolysis/gasification system was simulated using Aspen Plus® based on the experimental study of Arregi et al. [4]. In their experimental study, they carried out pyrolysis/gasification of a mixture of HDPE and biomass (i.e. pine sawdust) in a two-stage integrated system to investigate the influence of the synergic effect of multiple feedstocks on the gas production and deactivation of the catalyst.

The whole system consists of two separate reactors (Fig. 1). The first stage is a conical spouted bed reactor where pyrolysis reactions mainly occur. The feedstocks of HDPE and biomass are added into the first reactor continuously and they are decomposed into volatiles and char. Then, the char is removed from the products out of the first reactor and only volatiles are transferred to the second reactor. The second stage is a fluidised bed reactor where cracking and reforming reactions mainly occur. The volatiles from the first stage are further converted and reacted under the function of catalyst to generate various gas products. In addition to the two reactors, the system was originally designed to deal with multiple gasification agents such as air, H_2 and steam (Fig. 1). However, only steam was used as a gasification agent in Arregti et al. [4]. Other operating conditions and reactor dimensions are shown in Table 2, which will be used to develop models in Aspen Plus®.

Table 2
Summary of the experimental rig, feedstock information and operating conditions [4].

Parameter	Description
Experimental Rig	
First Stage	Pyrolysis – Conical Spouted Bed Reactor (CSBR) Dimensions not specified
Second Stage	Gasification – Fluidised Bed Reactor Dimensions: 38.1 mm × 440 mm (DxH)
Feedstocks	
Total mass flowrate (Biomass + Plastics)	0.75 g/min
Operating Conditions	
Reactor Temperature	Pyrolysis – 500 °C (CSBR) Reforming – 700 °C (Fluidised Bed Reactor)
Steam Flowrate	3 g/min
Ni catalyst	12.5 g

2.2. Assumptions

To develop the pyrolysis/gasification model, assumptions are made to ensure the accuracy of the process.

(1) The whole system operates at steady-state.
(2) Char is assumed only to consist of fixed carbon.
(3) The decomposition reactions in the first stage and cracking/reforming reactions in the second stage are all instantaneous. Only CO, CO_2, CH_4, C_6H_6, C_7H_8, C_6H_6O, $C_{10}H_8$, Char and H_2O are considered as intermediate or final products in this process.
(4) Reactors are considered to be operated under isothermal conditions.
(5) Uniform mixing is assumed to occur inside the fluidised bed reactor. Therefore, sufficient mass transfer and heat transfer can be realised.
(6) The temperature is consistent at any point inside the fluidised bed reactor.

2.3. Model development in Aspen Plus®

2.3.1. Components input and physical property calculation method selection

In this study, components such as biomass and HDPE are inputted as non-conventional solids. Specific properties parameters including proximate, ultimate and sulfur analysis of these non-conventional solids are inputted to ensure the normal calculation of relevant physical properties. Details of these three analyses can be found in Arregi et al. [4].

The normally used physical property calculation methods for simulating gasification of carbon-based material include Redlich-Kwong-Sovae (RKS) [2], Redlich-Kwong-Aspen equation (RK-Aspen) [1,32] and Redlich-Kwong-Sovae with Boston-Mathias alpha function (RKS-BM) [7]. According to the user guide of Aspen Plus®, these three methods are all suitable for processes such as gas processing, refinery and petrochemical applications. Both the RK-Aspen method and RKS-BM method are extensions of the RKS method. RK-Aspen is suggested to be used for processes with very high temperatures and pressure.

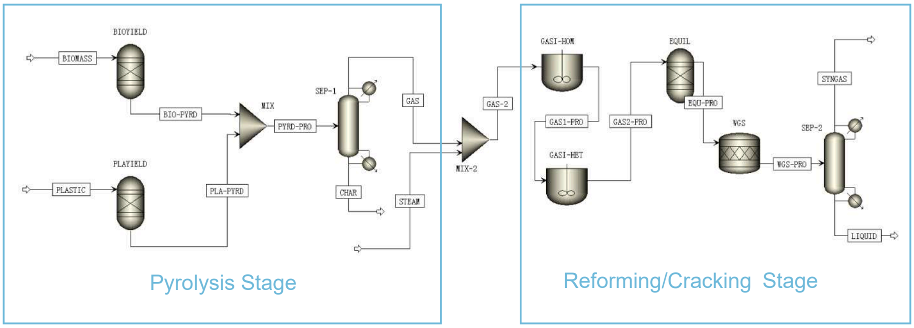

Fig. 2. Overview of flowsheet of developed model.

Table 3
Pyrolysis product yields used in RYield models [4].

Component	BIOYIELD (wt %)	PLAYIELD (wt%)
CO	0.0338	0
CO_2	0.0327	0
CH_4	0.0068	0.015
C_6H_6	0.1117	0.24625
C_7H_8	0.0007	0.24625
C_6H_6O	0.1649	0.24625
$C_{10}H_8$	0.1117	0.24625
CHAR	0.1731	0
H_2O	0.2536	0

Compared to RK-Aspen, RKS-BM has wider usability at all temperature and pressure ranges. Considering the process analysis in this study involving low-temperature range, RKS-BM is selected as the physical property calculation method. In addition, RKS-BM is also mostly used for the coal gasification process [7] and coal has similar element compositions compared to biomass and HDPE.

2.3.2. Pyrolysis stage

The flowsheet of the pyrolysis/gasification process is shown in Fig. 2. The pyrolysis stage is simulated using two **RYield** model blocks (i.e. **BIOYIELD** and **PLAYIELD**). In this study, the operating temperature of the pyrolysis stage is fixed at 500 °C, so the product yields of biomass and plastics pyrolysis should also keep constant when there is no temperature change. The product yields are directly inputted in the **RYield** model block to determine the reaction extent of pyrolysis process. The specific yields are shown in Table 3, which are adapted from the detailed experimental results of pyrolysis yields in Arregi et al. [4]. It is assumed that the yields of tar components of plastics pyrolysis are all the same. Then the pyrolysis products are transferred to the first separator (i.e. **SEP-1**) to remove the char content that is the carbon in solid status. Only volatiles are allowed to enter the following cracking and reforming stage.

It should be noted that the specific pyrolysis reactions were not simulated in this study. According to Arregi et al. [4], the pyrolysis and reforming stages occur in two different reactors. In the following process improvement analysis, the recycling of captured CO_2 and additional carbon stream are all injected into the reforming stage (i.e. the second reactor in real-life). In addition, only operating conditions of the reforming stage are changed for investigation and the operating conditions of the pyrolysis stage are fixed all the time, which means the yields of pyrolysis products will not change. Arregi et al. [4] provided detailed results of pyrolysis yields under a specific temperature. Therefore, simulation of pyrolysis stage is achieved by directly setting the same pyrolysis yields as presented in Arregi et al. [4]. This can simplify the whole model development and also ensure the accuracy of the developed model.

2.3.3. Reforming stage

The reforming stage is simulated using four model blocks (Fig. 2). The first two model blocks are ***RCSTR*** reactors (i.e. ***GASI-HOM*** and ***GASI-HET***), which are kinetic reactor blocks and require specific reaction kinetics to determine the reaction extent. ***GASI-HOM*** is used to simulate homogeneous reactions occurring inside the real fluidised bed reactor. The main reactions inside ***GASI-HOM*** contain a series of tar cracking reactions, water–gas-shift (WGS) reaction and steam-methane-reforming (SMR) reaction. The reaction kinetics used in ***GASI-HOM*** are derived from Abdelouahed et al. [1], Rafati et al. [32], Gerun et al. [19] and Jess [21].

$C_{10}H_8 \rightarrow 9C + \frac{1}{6}C_6H_6 + 3.5H_2$	$r_1 = 3.4 \times 10^{14} \exp(-\frac{350000}{RT}) C_{C10H8}^{1.6} C_{H2}^{-0.5}$	Rec (1)
$C_6H_6 + 2H_2O \rightarrow 1.5C + 2.5CH_4 + 2CO$	$r_2 = 4 \times 10^{16} \exp(-\frac{443000}{RT}) C_{C6H6}^{1.3} C_{H2O}^{0.2}$	Rec (2)
$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4$	$r_3 = 1.04 \times 10^{12} \exp(-\frac{247000}{RT}) C_{C7H7} C_{H2}^{0.5}$	Rec (3)
$C_6H_6O \rightarrow CO + 0.4C_{10}H_8 + 0.15C_6H_6 + 0.1CH_4 + 0.75H_2$	$r_4 = 1.0 \times 10^7 \exp(-\frac{100000}{RT}) C_{C6H6O}$	Rec (4)
$CO + H_2O \rightarrow CO_2 + H_2$	$r_5 = 5.2 \times 10^5 \exp(-\frac{102400}{RT}) C_{H2O} C_{CO}$	Rec (5)
$CH_4 + H_2O \rightarrow 3H_2 + CO$	$r_6 = 1.15 \times 10^{12} \exp(-\frac{39572}{RT}) C_{CH4}^{1.7} C_{O2}^{-0.8}$	Rec (6)

GASI-HET is used to simulate the heterogeneous reactions inside the fluidised bed reactor that are under the promotion effect of Ni-based catalyst. The main reactions inside ***GASI-HET*** include tar cracking reactions, WGS reaction, SMR reaction, water gas reaction and Boudouard reaction. The reaction kinetics used in ***GASI-HET*** are derived from El-Rub et al. [43], Rafati et al. [32] and Abdelouahed et al. [1]. It can be observed from the Reactions (7) to (14) that the activation energy of tar cracking and WGS reactions in ***GASI-HET*** are lower than that in the ***GASI-HOM***. This is becausethe function of Ni-based catalyst is to decrease the activation energy required by reactions.

$C_{10}H_8 \rightarrow 9C + \frac{1}{6}C_6H_6 + 3.5H_2$	$r_7 = 126.66 \exp(-\frac{61000}{RT}) C_{C10H8}$	Rec (7)
$C_6H_6 + H_2O \rightarrow 3C + 2CH_4 + CO$	$r_8 = 126.66 \exp(-\frac{61000}{RT}) C_{C6H6}$	Rec (8)
$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4$	$r_9 = 126.66 \exp(-\frac{61000}{RT}) C_{C7H7}$	Rec (9)
$C_6H_6O \rightarrow CO + 0.4C_{10}H_8 + 0.15C_6H_6 + 0.1CH_4 + 0.75H_2$	$r_{10} = 95798 \exp(-\frac{79000}{RT}) C_{C6H6O}$	Rec (10)
$CH_4 \rightarrow C + 2H_2$	$r_{11} = 0.01 \exp(-\frac{263000}{RT}) C_{CH4}$	Rec (11)
$CO + H_2O \rightarrow CO_2 + H_2$	$r_{12} = 5.2 \times 10^5 \exp(-\frac{50240}{RT}) C_{H2O} C_{CO}$	Rec (12)
$C + H_2O \rightarrow CO + H_2$	$r_{13} = 3 \times 10^{11} \exp(-\frac{310000}{RT}) C_{H2O}$	Rec (13)
$C + CO_2 \rightarrow 2CO$	$r_{14} = 4.364 \exp(-\frac{29844}{RT}) C_{H2O} C_{CO}$	Rec (14)

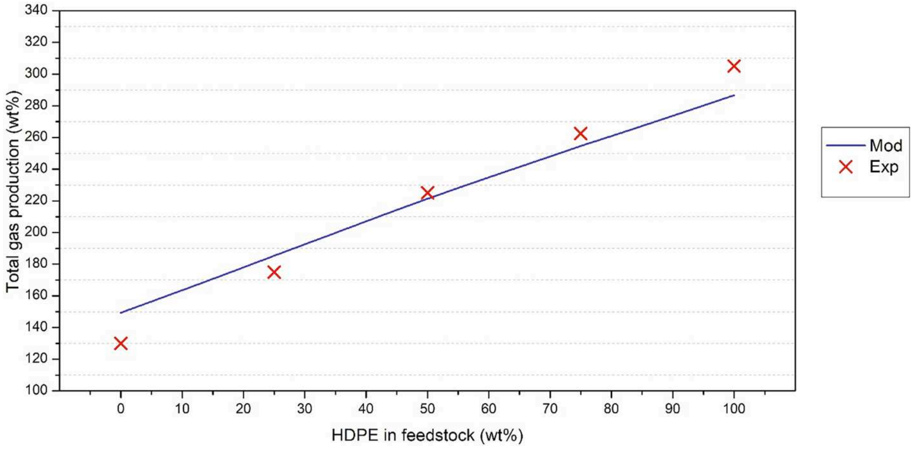

Fig. 3. Results of model validation changing feedstocks ratio.

Table 4
Total gas production and relative error between model predictions and experiments.

HDPE (wt %)	Biomass (wt %)	Model Predictions (wt %)	Experiment (wt %)	Relative Errors (%)
0	100	149.33	130.00	14.87
25	75	185.33	175.00	5.91
50	50	221.33	225.00	−1.63
75	25	254.67	262.50	−2.98
100	0	286.67	305.00	−6.01

Table 5
Gas compositions and relative error between model predictions and experiments.

HDPE wt%	Biomass wt%	Component	Model Predictions	Experiment	Relative Errors
0	100	H_2	67.97	65.51	3.75
		CO_2	27.53	30.18	−8.78
		CO	4.5	4.31	4.41
25	75	H_2	68.92	69.28	−0.52
		CO_2	25.43	24.47	3.92
		CO	5.65	6.25	−9.60
50	50	H_2	69.02	71.06	−2.87
		CO_2	24.38	22.88	6.55
		CO	6.60	6.06	8.91
75	25	H_2	69.33	72.00	−3.71
		CO_2	7.72	7.20	7.22
		CO	22.95	20.90	9.81
100	0	H_2	68.68	69.75	−1.53
		CO_2	8.85	9.10	−2.75
		CO	22.46	21.15	6.19

The third reactor (i.e. ***EQUIL***) is a ***RGibbs*** model block. The function of this model block is to make the product distribution of the previous two reactors further reach equilibrium. The system will adjust the yields of various products according to the principle of minimisation of Gibbs free energy. During model validation, the whole model was first run to check the results without the introduction of the fourth reactor. It was found that the CO composition was relatively higher and the CO_2 composition was lower, which means that the reaction extent of the WGS reaction was still not enough. Therefore, an extra WGS reaction is required to balance the compositions of CO and CO_2 in the product stream and a new ***RStoic*** model block ***WGS*** is used to achieve this function. Only WGS reaction is involved in this reactor and it is assumed that the conversion ratio of CO is 0.3. This conversion ratio is tested to have the lowest relative errors after a series of the attempt by changing the conversion ratio from 0 to 1.

To summarise, the four model blocks (i.e. ***GASI-HOM***, ***GASI-HET***, ***EQUIL*** and ***WGS***) work together to simulate the cracking and reforming stage of this pyrolysis/gasification system. Then, the final products go through another separator (i.e. ***SEP-2***) and the gas products such as CO, CO_2, CH_4 and H_2 are separated from the rest unreacted volatiles and gasification agent H_2O.

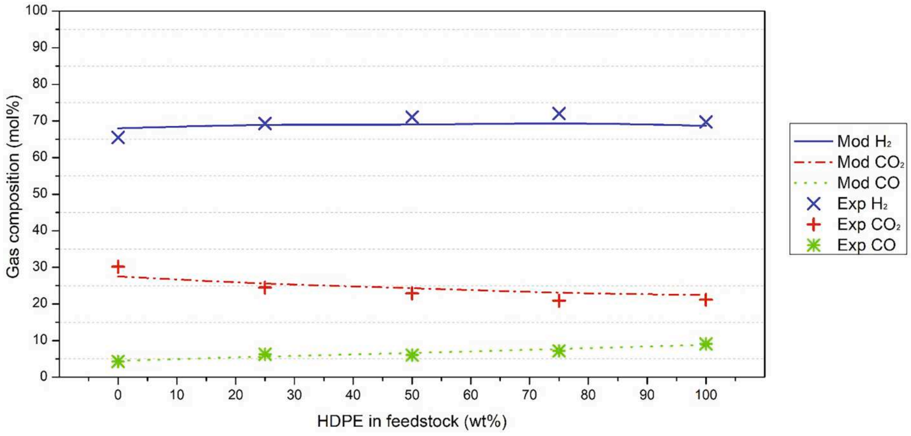

Fig. 4. Results of model validation of gas compositions of stream SYNGAS when changing feedstocks ratio.

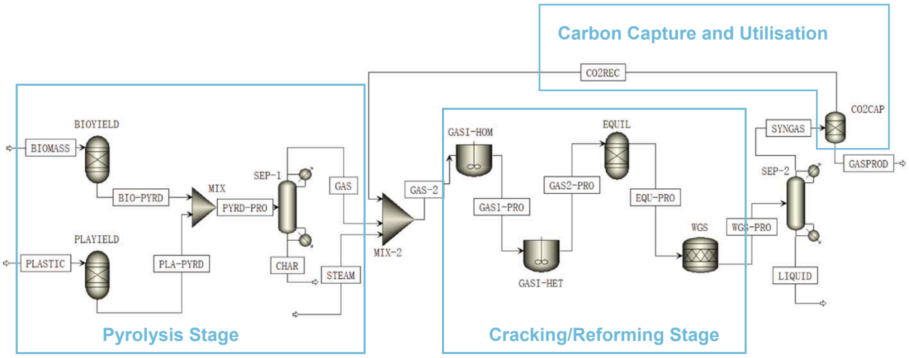

Fig. 5. Overview of flowsheet of improved model with CCU process.

2.4. Model validation

It has been mentioned in Section 2.1 that the experimental data from Arregti et al. (2017) is used for model validation. The model is simulated by inputting the same equipment dimension and operating conditions as provided in Table 2. The model prediction results of the total gas production and gas compositions under different biomass/plastics ratio are compared with the real experimental data to examine the accuracy of the developed model. The validation results of total gas production in stream **SYNGAS** (see Fig. 2) are shown in Fig. 3 and Table 4. The validation results of gas compositions are shown in Fig. 4 and Table 5.

From Arregi et al. [4], the total gas production is defined as the ratio of the number of gas products over the biomass and plastics feed on a mass basis, which is calculated using Eq (1).

$$P_{gas} = \frac{m_g}{m_0} \times 100 \tag{1}$$

where, P_{gas} = total gas production over feed (wt%),

m_g = mass flow of the gas products (g/min),

m_0 = mass flow of the feed of HDPE and biomass to the reactor (g/min).

From Fig. 3 and Table 4, it can be observed that when only biomass (i.e. 0 wt% HDPE, 100 wt% biomass) is used for pyrolysis/gasification, the relative error is 14.87 %, which may be caused by the system error of the experimental data. The relative errors of other conditions are all lower than 10 %.

From Fig. 4 and Table 5, the relative errors between model predictions (gas compositions of stream **SYNGAS** in Fig. 2) and experiment results are all lower than 10%, which can demonstrate that the developed model can predict the real yields of the pyrolysis/gasification process very well. The accuracy of this model is confirmed. Further research regarding the influence of applying CCU for the pyrolysis/gasification process is carried out based on this model. The condition of 50 wt% HPDE and 50 wt% biomass is selected as the base condition for further process analysis due to its relatively low errors of gas production and gas compositions.

3. Process improvement of applying CCU for pyrolysis/gasification

3.1. Flowsheet improvement

First of all, assumptions should be made and scopes about the process improvement should be clarified.

(1) Only CO_2 generated from reactions inside pyrolysis and cracking/reforming reactors are captured. The equivalent CO_2 emission from energy consumption to maintain the normal operation of pyrolysis/gasification process is neglected in this study.
(2) This is a simplified model for CCU that aims to investigate the influence of recycling captured CO_2 to the pyrolysis/gasification system on the product distribution. Therefore, no detailed flowsheet is developed for the carbon capture process specifically.
(3) It should be noted that it is not practical to make all the CO_2 be captured in reality. Normally, the capture level of the current carbon capture system is assumed to be 90 % [37,38]. In this study, it is assumed that all the captured CO_2 under the specific capture level is recycled into the pyrolysis/gasification system.

The new flowsheet for process improvement is shown in Fig. 5. According to the definitions above, a new separator (i.e. ***CO2CAP***) is added after the final gas products stream (i.e. **SYNGAS** in Fig. 2). This separator functions as the process of carbon capture. The split ratio of this separator represents the capture level of the carbon capture process, which can determine the amount of CO_2 back to the pyrolysis/gasification system. For example, when the split ratio is 0.9, it means that 90 % of the CO_2 in the SYNGAS stream is captured and recycled to the reforming stage. Stream ***GASPROD*** becomes the new final gas product stream. Then, the stream of captured CO_2 ***CO2REC*** is recycled to the cracking/reforming stage to serve as a new gasification agent for further utilisation.

3.2. Definition of performance index

CO_2 is captured and recycled to the pyrolysis/gasification process to serve as the second gasification agent. It is vital to find out how much recycled CO_2 is reacted in the cracking/reforming stage, which can reflect the extent of CO_2 utilisation. Therefore, an index is defined to calculate the conversion extent of the recycled CO_2. The equation to calculate the CO_2 conversion is shown in Eq (2).

$$\mathrm{CONV}_{CO2} = \frac{(W_{CCUCO} - W_{CO})}{W_{RecCO2}} \times \frac{\vartheta_{CO2} M_{CO2}}{\vartheta_{CO} M_{CO}} \tag{2}$$

where CONV_{CO2} = the conversion of the recycled CO_2,

W_{CCUCO} = the mass yield of CO in the gas product stream with recycled CO_2 stream, g/min.

(mass flowrate of CO in stream ***GASPROD*** in Fig. 5)

W_{CO} = the mass yield of CO in the gas product stream without recycled CO_2 stream, g/min.

(mass flowrate of CO in stream ***SYNGAS*** in Fig. 2)

W_{RecCO2} = the mass of CO_2 that is recycled into the system, g/min.

(mass flowrate of CO_2 in stream ***CO2REC*** in Fig. 5)

ϑ_{CO2} = Stoichiometry of CO_2,

ϑ_{CO} = Stoichiometry of CO,

M_{CO2} = Molecular weight of CO_2, g/mol.

M_{CO} = Molecular weight of CO, g/mol.

Eq (2) is derived from the following procedures:

It can be observed from Reactions (1) to (14) in section 2.3.3 that CO_2 participates in two reactions in the cracking/reforming stage, which

Table 6
Plan of process analysis.

Case of Process analysis	Split ratio of ***CO2CAP***	Reforming temperature (°C)	S/F ratio (Mass basis)
Section 4.2	0 ~ 0.9	700	4
Section 4.3	0.9	400 ~ 1000	4
Section 4.4	0.9	700	2 ~ 10

are the WGS reaction (Reaction 5 under catalyst and Reaction 12 without catalyst) and Boudouard reaction (Reaction 14). When the captured CO_2 is added into the system, it will influence gas production through these two reactions. Therefore, an integrated reaction (i.e. Reaction 15) is developed by combining the reverse WGS and Boudouard reactions to reflect the conversion of recycled CO_2.

$2CO_2 + H_2 + C \rightarrow 3CO + H_2O$ Rec (15)

The influence of other reactions on the yield of CO is minimal after recycling captured CO_2, which can be ignored. Based on the mass balance of the chemical formula, the amount of reacted CO_2 is calculated depending on the change of CO yield before and after recycling CO_2 according to Reaction 15. The ϑ_{CO2} and ϑ_{CO} in Eq (2) refer to the stoichiometry in Reaction 15. Then the CO_2 conversion is calculated using the amount of reacted CO_2 to divide the total amount of recycled CO_2.

4. Process analysis of pyrolysis/gasification process with CCU

4.1. Plan of process analysis

Detailed process analysis is carried out to investigate the influence of recycling captured CO_2 when various operating conditions are changed. Three operating conditions including recycled CO_2 amount, reforming temperature and S/F ratio are changed. The specific simulation plan is shown in Table 6.

The amount of recycled CO_2 is controlled by the split ratio of separator ***CO2CAP***. The total mass flowrate of the mixture of biomass and HDPE is 0.75 g/min. Therefore, the corresponding steam mass flowrate can be calculated according to the S/F ratio. The other operating conditions are fixed and are shown as follows: feedstocks ratio (50 wt% biomass / 50 wt% HDPE) and pyrolysis temperature of 500 °C.

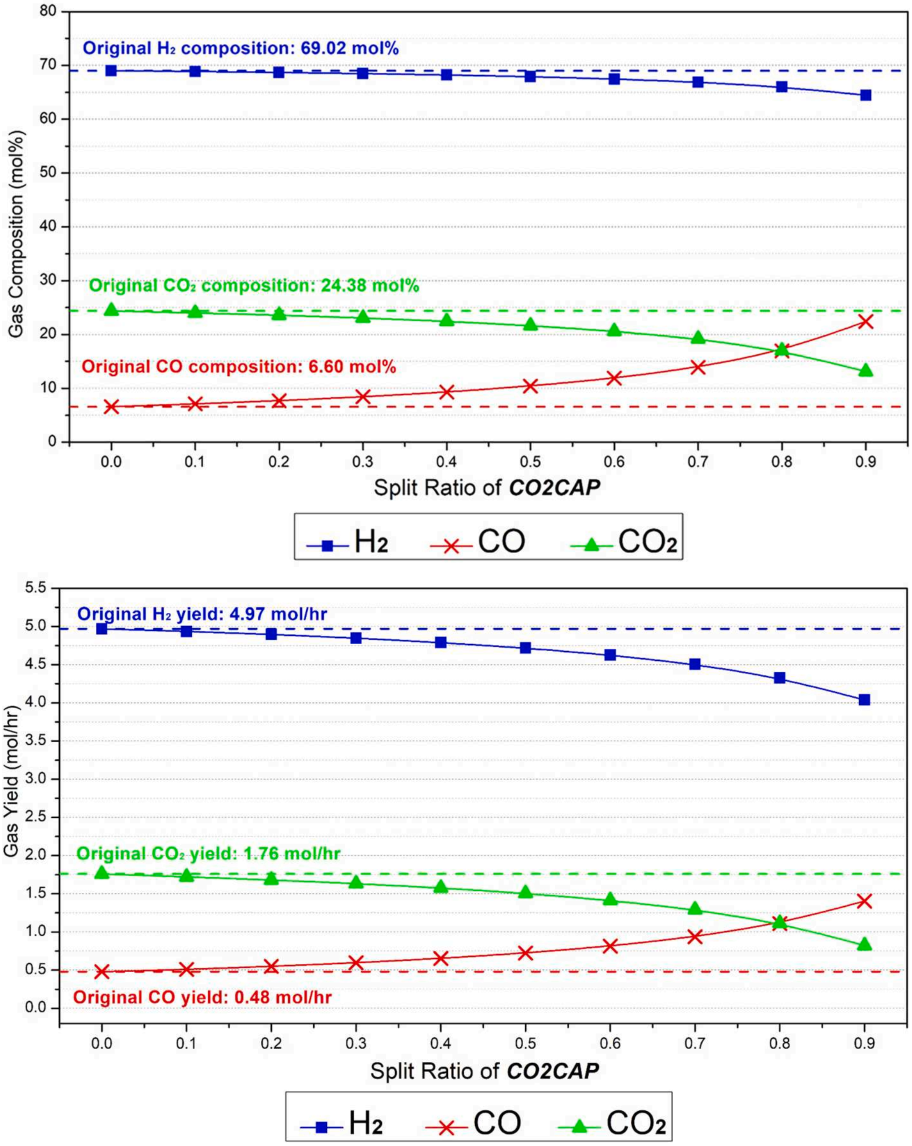

Fig. 6. Influence of CO_2 recycle amount on the gas production.

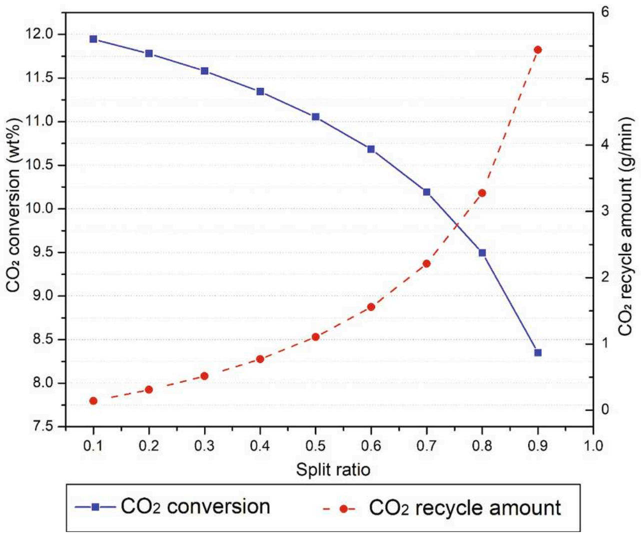

Fig. 7. Influence of CO_2 split ratio on the CO_2 conversion.

4.2. Process analysis of changing recycled CO_2 amount

4.2.1. Influence of CO_2 recycle amount on product gas compositions and yields

CO_2 is captured and recycled to the reactor to serve as the second gasification agent. Process analysis is carried out by changing the split ratio of separator ***CO2CAP*** from 0 to 0.9 (i.e. capture level changes from 0 % to 90 %) to control the amount of CO_2 recycling to the system. The results of gas compositions and yields are shown in Fig. 6.

From Fig. 6(a) and 6(b), when the split ratio is 0, which means no captured CO2 is recycled to the reforming stage. The H_2 composition and yield in the **GASPROD** stream are 69.02 mol% and 4.97 mol/h respectively. The CO_2 composition and yield are 24.38 mol% and 1.76 mol/hr. The CO composition and yield are 6.60 mol% and 0.48 mol/hr. With the spit ratio increase, more CO_2 is recycled to the reforming stage. The H_2 composition and yield keep decreasing to reach 64.45 mol% and 4.04 mol/hr until the split ratio is 0.9. The composition and yield of CO_2 also decrease continuously with increase in split ratio (i.e. 13.15 mol% and 0.82 mol/hr at 0.9 split ratios). Different from H_2 and CO_2, the composition and yield of CO keep increasing with the increase of split ratio. To summarise the gas production of three gas products, it can be concluded that the H_2 and CO_2 production are restricted and the CO production is promoted when the captured CO_2 is recycled to serve as the second gasification agent. This result is consistent with the conclusion of using CO_2 as a gasification agent by Shen et al. [36].

The effect of the carbon capture process is obvious. The CO_2 compositions in the gas products decrease from 24.38 mol% to 13.15 mol% after 90% of CO_2 is captured and recycled. This demonstrates the benefit of applying CCU for pyrolysis/gasification process to reduce CO_2 emissions. To further decrease the CO_2 composition, more CO_2 should be converted during the reforming stage, thus increasing carbon conversion correspondingly. How to increase the carbon conversion will be discussed in the following sections.

The results that H_2 production is restricted after applying CCU are consistent with our original prediction. Fortunately, the reduction is not so serious after a demonstration from simulation results. From Fig. 6b, when 90 % of CO_2 is recycled (i.e. split ratio = 0.9), the H_2 yield decreases 23 percent from 4.97 mol/hr to 4.04 mol/hr. The H_2 production can still maintain a relatively high level. To further relieve the reduction of H_2 production, the catalyst is a key factor to promote the gas production of pyrolysis/gasification process [10]. It is suggested to use a highly efficient catalyst to offset the influence of CCU.

Production of CO is promoted significantly after applying CCU. From Fig. 6b, with a split ratio increase from 0 to 0.9, the CO yield increases 192 percent from 0.48 mol/hr to 1.40 mol/hr. The CO production is more sensitive to recycled captured CO_2 compared to H_2. This is because when per mole of H_2 is consumed and three moles of CO are generated simultaneously according to Reaction (15). Therefore, the recycled CO_2 has an ideal effect to control the H_2/CO ratio of the gas products. The H_2/CO ratio changes with a wide range from 10.46 to 2.88 when the split ratio changes from 0 to 0.9. The H_2/CO ratio can be changed with a wider range if applying CCU is co-operated with configuring operating conditions of the process. For some industry synthesis processes, it is crucial to control the H_2/CO ratio at a specific range or value. For example, Fischer-Trposch (F-T) synthesis process requires the H_2/CO to be at 2 for liquid fuel synthesis. The syngas for carbonyl synthesis requires the H_2/CO ratio to be as low as possible [18]. These are all potential applications to apply CCU for pyrolysis/gasification process due to its flexible control of the H_2/CO ratio.

4.2.2. Influence of recycled CO_2 amount on CO_2 conversion

The reason to introduce CO_2 conversion is to evaluate how much recycled CO_2 is reacted, which reflects the CO_2 treatment capability of the system and the extent of CO_2 utilisation. The CO_2 conversion and CO_2 recycle amount are calculated according to Eq (2). The results of the CO_2 conversion are shown in Fig. 7. The CO_2 conversion changes from 11.95 wt% to 8.35 wt% when the split ratio increases from 0.1 to 0.9. The CO_2 recycle amount refers to the W_{RecCO2} in Eq(2) to represent the amount of recycled CO_2 to the reforming stage. The CO_2 recycle amount keeps increasing from 0.14 g/min to 5.44 g/min. In summary, with split ratio increase, the CO_2 recycle amount should increase. However, the treatment capability of a pyrolysis/gasification system has a limitation and excessive recycled CO_2 can result in low CO_2 conversion consequently.

To improve the CO_2 conversion, the following two methods could be considered:

(1) To change the operating conditions of the pyrolysis/gasification system to be more suitable for the conversion of CO_2 is a useful option. In this study, the influences on the CO_2 conversion by changing operating reforming temperature and steam to feed ratio are investigated and will be introduced in the following sections. However, it is not wise to increase CO_2 conversion only by changing operating conditions. According to Reaction (15), H_2 is consumed when CO_2 is recycled and reacted. A higher CO_2 conversion may lead to insufficient H_2 production in the system. Therefore, it is necessary to balance the H_2 production and CO_2 conversion when changing operating conditions.

(2) To add more solid carbon in the reforming stage of pyrolysis/gasification system is an effective method to improve carbon conversion. From Reaction (15), more solid carbon in the reforming stage can help to substitute H_2 to react with CO_2, thus protecting H_2 production and promoting CO_2 conversion.

In reality, char or other carbon-based material can be added into the reforming stage to serve as a good source of solid carbon. For example, it is suggested to use a Ni-based catalyst that is attached to the activated carbon or bio-char support to improve the H_2 production and CO_2 conversion simultaneously [9]. In addition, the synergic effect between two gasification agents (i.e. steam and CO_2) can help to activate char effectively [32,36], which can improve the pore structure of the char. The activated char can reach the same standard as activated carbon. This can provide extra economical value when applying CCU for pyrolysis/gasification process.

4.2.3. Process analysis of influence of solid carbon on CO_2 conversion

To explore the influence of solid carbon on CO_2 conversion, tests have been performed to add the separated char after pyrolysis stage (i.e. the carbon content in stream **CHAR** in Fig. 5) into the reforming stage. However, the improvement in CO_2 conversion is not obvious, so the

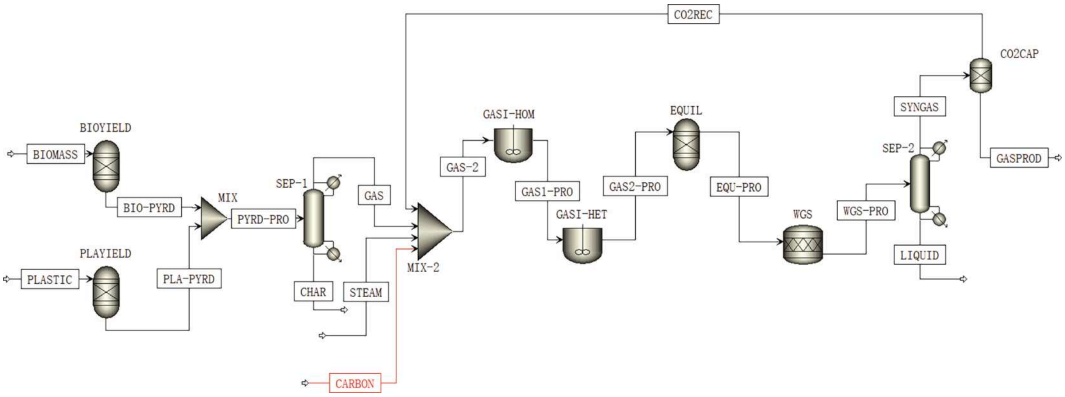

Fig. 8. Process analysis to investigate the impact of adding solid carbon on CO_2 conversion.

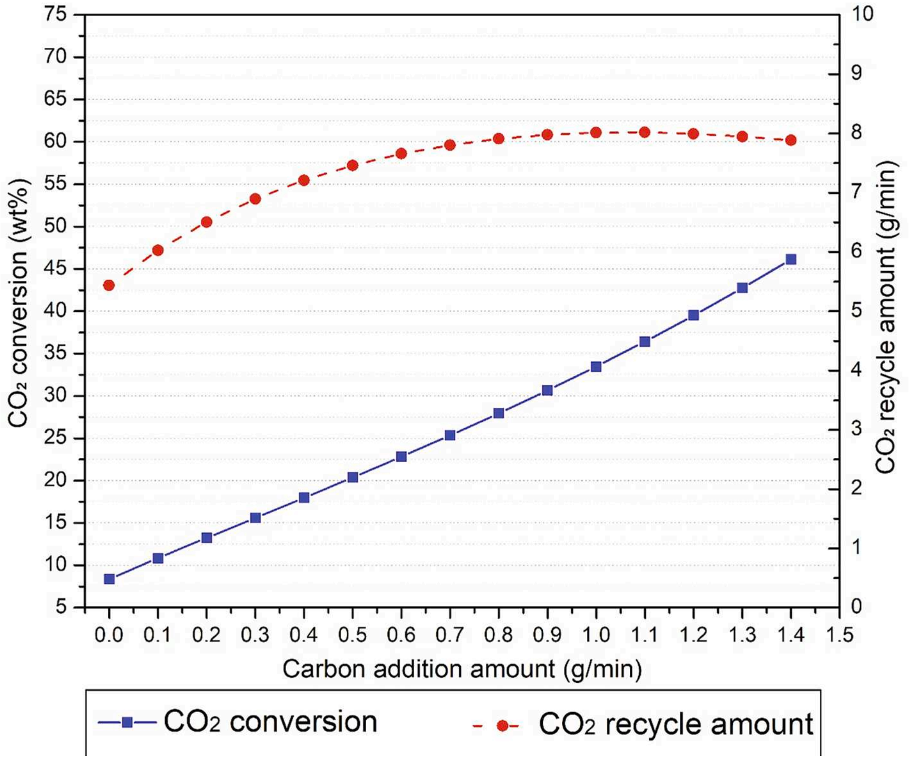

Fig. 9. Influence of solid carbon on CO_2 conversion.

results are not exhibited. The probable reason may be that the yield of char after pyrolysis is very low according to Table 3, which has limited influence on the CO_2 conversion.

To have a better understanding of the influence of soild carbon, a process analysis was carried out by adding a new stream (i.e. the stream **CARBON** in red colour in Fig. 8) consisting of solid carbon to the reforming stage through simulation. The split ratio of **CO2CAP** is set as 0.9 and the other operating conditions are the same as process analysis in section 4.2.1 The CO_2 conversion and CO_2 recycle amount are tested by changing amount of solid carbon (i.e. from 0 g/min to 1.4 g/min) entering the reforming stage. The results are shown in Fig. 9.

From Fig. 9, the CO_2 conversion is 10.85 wt% when 0.1 g/min carbon is added in the reforming stage, which is higher than the CO_2 conversion without carbon addition (i.e. 8.35 wt%). With more carbon is added, the CO_2 conversion keeps increasing to 46.11 wt% when 1.4 g/min solid carbon is added. This is consistent with our conclusion in section 4.2.2.

When comes to the CO_2 recycle amount, it keeps increasing when carbon addition increases from 0 g/min (i.e. 5.44 g/min CO_2 recycle) to 0.8 g/min (i.e. 7.97 g/min CO_2 recycle). After that point, with carbon addition further increasing to 1.4 g/min, the CO_2 recycle becomes stable at around 8.01 g/min and even decreases slightly eventually at 7.89 g/min. To explain this, reaction (15) consists of the reverse of WGS reaction and Boudouard reaction (Reaction 14). The addition of carbon promotes the reaction extent of Boudouard reaction effectively. Consequently, more CO_2 is consumed and more CO is generated. The increasing amount of CO and insufficient amount of CO_2 promotes the reaction equilibrium of WGS reactions (Reactions 5 and 12) to move forward to generate more CO_2. Consequently, the amount of newly generated CO_2 due to WGS reactions and the amount of converted CO_2 due to Boudouard reaction both increase. However, the newly generated CO_2 surpasses the amount of converted CO_2 temporarily to increase CO_2 recycle amount. The recycled CO_2 keeps increasing with more carbon addition until the amount of gasification agent H_2O is not enough to maintain forward WGS reaction to generate more CO_2. Then, the Boudouard reaction will be dominant and the amount of converted CO_2

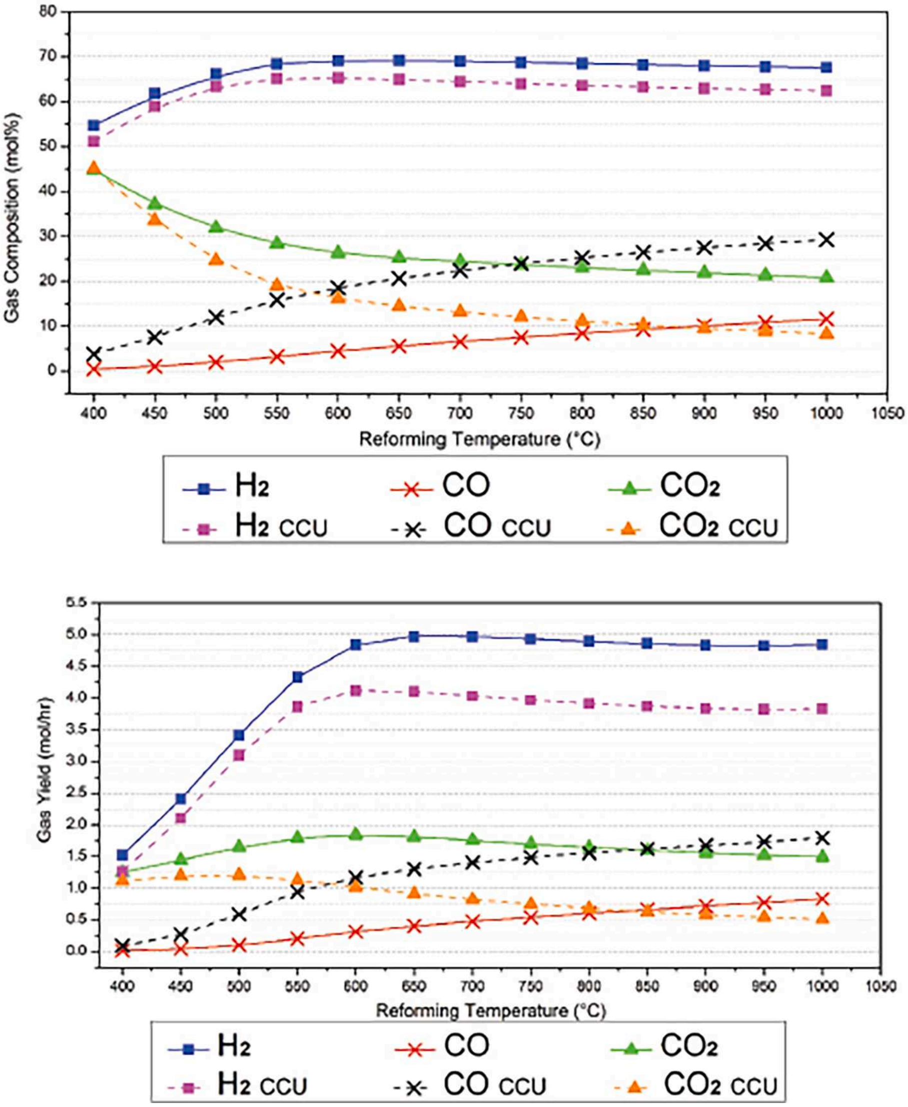

Fig. 10. Influence of reforming temperature on the gas production.

equals or even surpasses a little compared to the newly generated CO_2.

It can be concluded that the addition of solid carbon can promote the CO_2 conversion significantly. Although the recycled CO_2 also increases with more carbon, it is believed that cooperation of solid-carbon addition and changing operating conditions (e.g. can restrict the amount of H_2O to inhibit forward WGS reaction) can further decrease the CO_2 recycled and increase CO_2 conversion.

4.3. Process analysis to investigate the impact of changing reforming temperature

4.3.1. Influence of reforming temperature on the product gas compositions and yields

The temperatures of four model blocks in Fig. 5 of the reforming stage (i.e. ***GASI-HET***, ***GASI-HOM***, ***EQUIL*** and ***WGS***) are changed together to simulate the change of reforming temperature. The gas production under different reforming temperatures with and without CCU are compared. The results of product gas compositions and gas yields are shown in Fig. 10.

From Fig. 10(a) and (b), when CCU is not applied, the H_2 yield is 1.52 mol/hr at 400 °C and it keeps increasing to the peak yield at 4.98 mol/hr at 700 °C. Then, a further increase in temperature results in a slight decrease in H_2 yield and it is 4.85 mol/hr at 1000 °C. The H_2 composition changes with a similar trend as H_2 yield under the influence of reforming temperature. The yield of CO_2 increases from 1.25 mol/hr at 400 °C to 1.84 mol/hr at 600 °C and then it keeps decreasing to 1.49 mol/hr at 1000 °C. The CO_2 composition is very high at 44.83 mol% under 400 °C due to the low gas yields of H_2 and CO. Then, the CO_2 composition keeps decreasing with the increase of reforming temperature. The CO yield is elevated continuously from 0.01 mol/hr at 400 °C to 0.83 mol/hr at 1000 °C.

When the CCU is applied and CO_2 is recycled to the reforming stage, the H_2 yield increases from 1.26 mol/hr (i.e. 400 °C) to 4.12 mol/hr (i.e. 600 °C) and then decreases to 3.83 mol/hr (i.e. 1000 °C). The H_2 composition has a similar trend as H_2 yields. It firstly increases from 51.11 mol% at 400 °C to 65.31 mol% at 600 °C, then the H_2 starts to decrease and reaches 62.45 mol% at 1000 °C. The CO_2 yield firstly increases from 1.11 mol/hr at 400 °C to 1.20 mol/hr at 500 °C and then decreases to 0.51 mol/hr at 1000 °C. The CO_2 composition keeps decreasing from 45.09 mol% to 8.28 mol% from 400 to 1000 °C. The CO composition and yield all keep increasing from 3.80 mol% and 0.09 mol/hr at 400 °C to 29.27 mol% and 1.80 mol/hr at 1000 °C.

The influence of reforming temperature on gas production can be explained from two aspects: reaction kinetics and thermodynamics. When the temperature is relatively low around 400 °C, the reaction rates are very low, resulting in low reaction extent and low product gas yields.

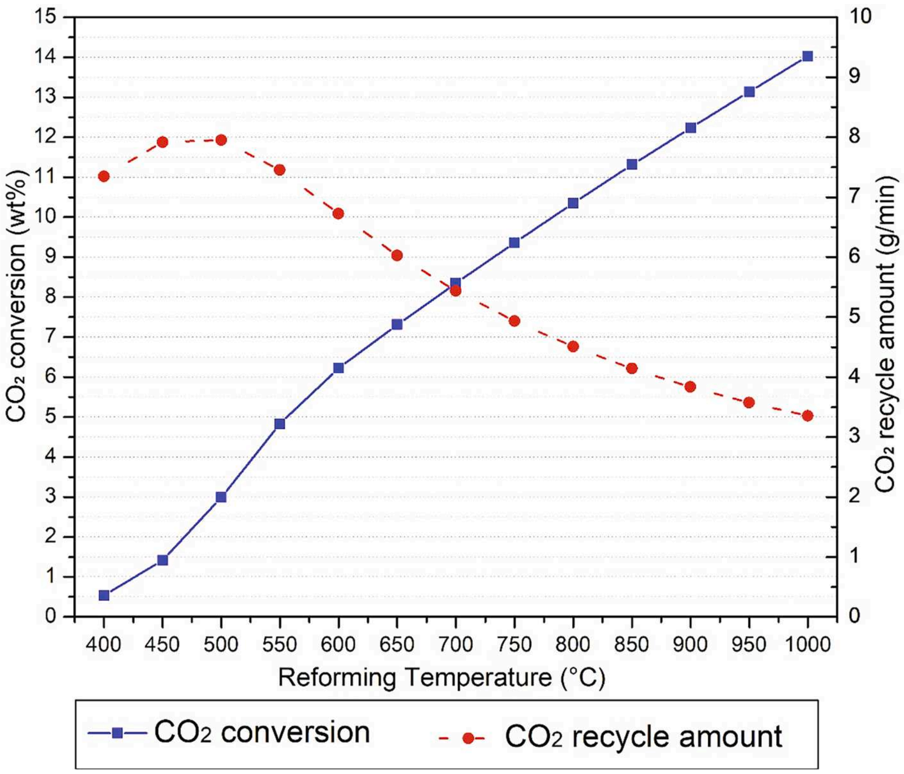

Fig. 11. Influence of reforming temperature on the CO_2 conversion.

With temperature increase, the reaction rates increase to make higher product yields possible. On the other hand, thermodynamics also influences gas production. Reactions such as Water-Gas reaction (Reaction 13), Boudouard reaction (Reaction 14) and SMR reaction (Reaction 6) are all endothermic [39]. According to the Le Chatelier principle, the reaction equilibrium of endothermic reaction moves towards generating more products with temperature increase. Combining the effects of both reaction kinetics and thermodynamics can help to explain the increasing yields of gas products around 400 to 600 °C very well. After 600 °C, both H_2 yield and CO_2 yield decrease slightly. This is because the WGS reaction is an exothermic reaction [39], the reaction equilibrium moves towards generating less H_2 and CO_2 with temperature increase.

To compare the two cases (with CCU and without CCU), it can be found that the compositions and yields of H_2 with CCU are all lower than that without CCU. When there is no CO_2 recycle, the compositions and yields of CO_2 are always higher than that of CO from 400 to 1000 °C. However, the composition and yield of CO exceed that of CO_2 at 600 °C after CO_2 is recycled in the system. CO production is promoted a lot and CO_2 production is restricted obviously after CO_2 is recycled. These results are consistent with the conclusions in section 4.2.1. In addition, the differences in the gas yield between two situations (i.e. with CCU and without CCU) are also changed with temperature. For example, at 400 °C, the difference in H_2 yield is 0.26 mol/hr. At 1000 °C, the difference in H_2 yield increases to 1.02 mol/hr. The same trends can also be observed in CO and CO_2 production. This is because the reaction extent is higher under higher temperatures, thus more recycle CO_2 is being reacted.

In summary, to ensure the H_2 production, a relatively high reforming temperature (e.g. 600 ~ 700 °C) is suggested. However, the reforming temperature should not be above 750 °C, which results in lower H_2 production. In addition, if unrenewable energy is used to supply energy for the whole pyrolysis/gasification system, more CO_2 emissions will be released due to increasing energy consumption requirements under higher temperatures.

4.3.2. *Influence of reforming temperature on the CO_2 conversion*

The results of the influence of reforming temperature on CO_2 conversion are shown in Fig. 11. With a temperature increase from 400 °C to 1000 °C, the CO_2 conversion increases from 0.53 wt% to 14.03 wt%. The recycled CO_2 firstly increases from 400 °C at 7.34 g/min to 500 °C at 7.95 g/min, then it keeps decreasing to 3.35 g/min as temperature further increases. The probable reason that recycled CO_2 is increased before 500 °C is because reaction rates increase to promote the reaction extent.

It can be concluded that a higher reforming temperature is helpful to improve CO_2 conversion. Reaction (15) consists of Boudouard reaction and reverse WGS reaction. These two reactions are all endothermic reactions. Therefore, with temperature increase, the reaction equilibrium of Reaction (15) moves toward consuming more CO_2 and generating more CO. Therefore, the recycled CO_2 decreases (after 500 °C) and CO_2 conversion increases. However, it is not wise to increase the reforming temperature excessively to chase higher CO_2 conversion. The reasons are shown as follows: (i) 1000 °C is already a high temperature for pyrolysis/gasification process. The CO_2 conversion is still not so high only at 14.03 wt% under 1000 °C. Therefore, further increased temperature has a limited promotion on the CO_2 conversion and H_2 production will be further restricted. (ii) To let the reactor operate at a higher reforming temperature, excessive energy is required [25]. The excessive consumed energy will result in extra CO_2 emissions if unrenewable energy is used, which violates the initial motivation to apply CCU for pyrolysis/gasification process.

4.4. *Process analysis to investigate the impact of changing steam to feed ratio*

4.4.1. *Influence of steam-to-feed ratio on the product gas compositions and yields*

The product distribution of pyrolysis/gasification can be influenced by the amount of gasification agent. In this study, the S/F ratio is changed from 2 to 10 to investigate the influence on the gas production

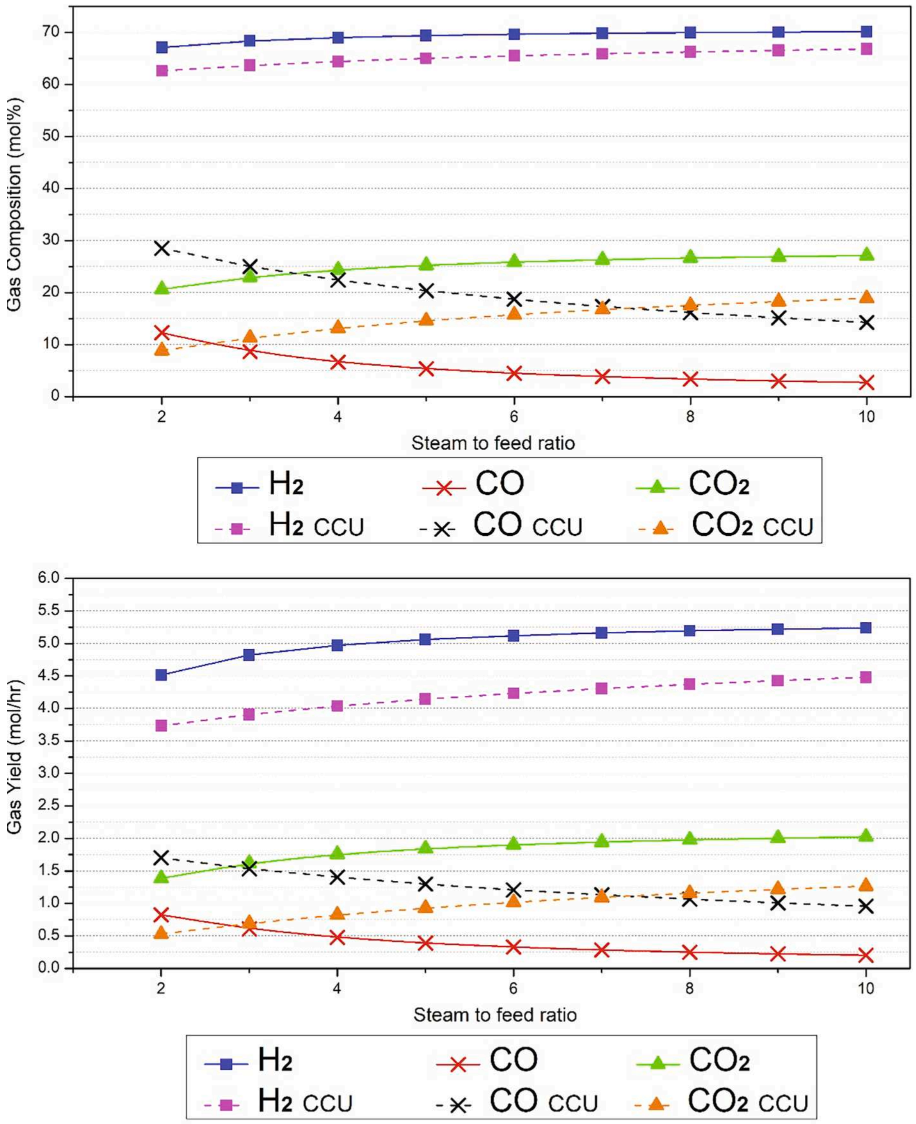

Fig. 12. Influence of S/F ratio on the product gas production.

with and without the CCU process. The results of product gas compositions and gas yields are shown in Fig. 12.

From Fig. 12(a) and (b), when the CO_2 is not recycled to the system, the H_2 compositions and yields increase from 67.13 mol%, 4.51 mol/hr (i.e. S/F = 2) to 70.18 mol%, 5.24 mol/hr (i.e. S/F = 10). The CO_2 compositions and yields also keep increasing from 20.59 mol%, 1.38 mol/hr (i.e. S/F = 2) to 27.12 mol%, 2.02 mol/hr (i.e. S/F = 10). On the contrary, the CO compositions and yields keep decreasing from 12.28 mol%, 0.83 mol/hr (i.e. S/F = 2) to 2.70 mol%, 0.20 mol/hr (i.e. S/F = 10).

After CO_2 is recycled to the pyrolysis/gasification system, the H_2 compositions and yields continuously increase from 62.61 mol%, 3.76 mol/hr (i.e. S/F = 2) to 66.83 mol%, 4.48 mol/hr (i.e. S/F = 10). The CO_2 compositions and yields keep increasing from 8.85 mol%, 0.53 mol/hr (i.e. S/F = 2) to 18.90 mol%, 1.27 mol/hr (i.e. S/F = 10). On the contrary, the CO compositions and yields keep decreasing from 28.53 mol%, 1.70 mol/hr (i.e. S/F = 2) to 14.27 mol%, 0.96 mol/hr (i.e. S/F = 10).

Gasification agent H_2O serves as reactant in a series of reactions such as tar cracking reaction (Reaction (2)), WGS reaction (Reaction 5), Water-gas reaction (Reaction 13) and SMR reaction (Reaction 6). According to the Le Chatelier principle, when more reactants are introduced into the system, the reaction equilibrium moves towards generating more products. Therefore, these reactions are all promoted to generate more products. Because the content of CH_4 and solid carbon in the system is very low in this study, the WGS reaction dominates the product distribution. With more H_2O added into the system, more CO is consumed and more H_2 as well CO_2 is generated consequently. This is consistent with the results in Fig. 12(a) and (b) that the production of H_2 and CO_2 are promoted but the production of CO is restricted.

To compare the influence of the S/F ratio on the gas production with and without CCU, lower H_2 composition and yield are observed after CO_2 is recycled. With the S/F ratio increase, the CO_2 compositions and yields are always higher than that of CO when no CO_2 is recycled. This is different after CO_2 is recycled, the compositions and yields of CO are higher than that of CO_2 when the S/F ratio is lower than 7. When the S/F ratio is higher than 7, the compositions and yields of CO are lower than that of CO_2. Therefore, the S/F ratio 7 is the key point that the H_2O content is sufficient to make the forward reaction of WGS reaction take dominant to offset the influence of recycled CO_2. When the S/F ratio is lower than 7, CO_2 takes the main role to move the reaction equilibrium to generate more CO. When the S/F ratio is higher than 7, H_2O takes the main role to move the reaction equilibrium to generate more CO_2.

In summary, to ensure H_2 production, a relatively low S/F ratio is

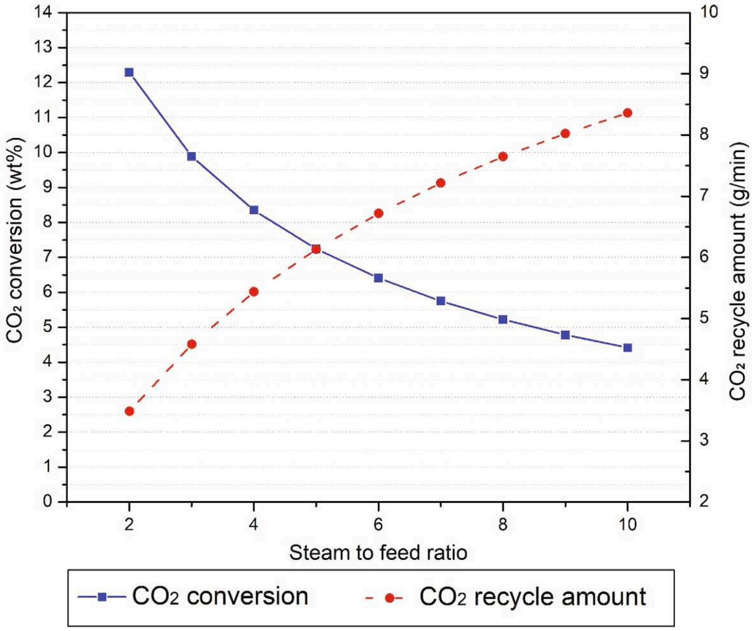

Fig. 13. Influence of S/F ratio on CO_2 conversion.

suggested. Because the changing amount of steam used for gasification has less influence on changing the H_2 yield. The S/F ratio at around 3 ~ 4 is adequate to ensure a relatively high H_2 production. The other reasons to use a low S/F ratio to achieve high CO_2 conversion will be discussed in the following section.

4.4.2. Influence of steam-to-feed ratio on the CO_2 conversion

From Fig. 13, when the S/F ratio increases from 2 to 10, the CO_2 conversion keeps decreasing from 12.29 wt% to 4.42 wt% and the recycled CO_2 keeps increasing from 3.48 g/min to 8.36 g/min. According to Reaction (15), with more H_2O existing in the system, the reaction equilibrium moves towards generating more CO_2. Therefore, less CO_2 is converted to CO and more CO_2 is captured and recycled. This is consistent with the previous conclusion that higher steam ratio results in lower CO production but higher CO_2 production.

A higher S/F ratio makes CO_2 conversion lower so less H_2O should be used for pyrolysis/gasification process. The benefits of changing the S/F ratio to improve CO_2 conversion are shown as follows: (1) Compared to changing the reforming temperature, it is more energy-efficient and energy-saved to change the amount of gasification agent (i.e·H_2O) to control the H_2/CO by influencing CO_2 conversion. This is useful to guide future practical applications. (2) As mentioned before in section 4.2.3, the cooperation of carbon addition and changing the amount of H_2O used in the reforming stage can help to improve the CO_2 conversion obviously. A relatively low S/F ratio is beneficial to restrict the forward WGS reaction to decrease CO_2 recycle amount.

5. Conclusion

In this paper, a model for a two-stage pyrolysis/gasification system was developed using Aspen Plus® to simulate the pyrolysis/gasification of biomass and plastics. The developed model was validated successfully compared with the real-life experimental data. The model was then improved by applying CCU for pyrolysis/gasification process. Process analysis was carried out to investigate the influence of recycling captured CO_2 to the pyrolysis/gasification system on the gas production and CO_2 conversion when changing various operating conditions (e.g. recycled CO_2 amount, reforming temperature and S/F ratio). Simulation results indicated that: (i) Recycling captured CO_2 to the reforming stage restricts the production of H_2 and CO_2 but CO production is promoted; (ii) Applying CCU for pyrolysis/gasification is effective to control the H_2/CO ratio, which is useful for specific synthesis process (e.g. F-T synthesis process and carbonyl synthesis); (iii) When increasing recycled CO_2 amount, the CO_2 conversion of captured CO_2 decreases. When increasing reforming temperature, the CO_2 conversion increases. When increasing the S/F ratio, the CO_2 conversion decreases; (iv) To achieve a high CO_2 conversion, it is suggested to add solid carbon (e.g. bio-char or carbon-based catalyst) in the reforming stage and adjust the operating conditions (i.e. relatively high reforming temperature (e.g. 600 ~ 700 °C) and low S/F ratio (e.g. 3 ~ 4)) simultaneously. The findings in this paper will be very useful for future large-scale commercial deployment of pyrolysis/gasification with CCU.

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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References

[1] Abdelouahed L, Authier O, Mauviel G, Corriou JP, Verdier G, Dufour A. Detailed modelling of biomass gasification in dual fluidized bed reactors under Aspen Plus. Energy Fuels 2012;26:3840–55.

[2] Adeyemi I, Janajreh I. Modeling of the entrained flow gasification: Kinetics-based ASPEN Plus model. Renewable Energy 2015;82:77–84.

[3] Amoodi NA, Kannan P, Shoaibi AA, Srinivasakannan C. Aspen Plus simulation of polyethylene gasification under equilibrium conditions. Chem Eng Commun 2013;200:977–92.

[4] Arregi A, Amutio M, Lopez G, Artetxe M, Bilbao J, Olazar M. Hydrogen-rich gas production by continuous pyrolysis and in-line catalytic reforming of pine wood waste and HDPE mixtures. Energy Convers Manage 2017;136:192–201.

[5] Association of Plastic Manufacturers. Plastics – the Facts 2018: An analysis of Euopean plastics production, demand and waste data. accessed on 1st July 2021, https://www.plasticseurope.org/application/files/6315/4510/9658/Plastics_the_facts_2018_AF_web.pdf; 2018.
[6] Babaei K, Bozorg A, Tavasoli A. Hydrogen-rich gas production through supercritical water gasification of chicken manure over activated carbon/ceria-based nickel catalysts. J Anal Appl Pyrol 2021;159:105318.
[7] Begum B, Rasul MG, Akbar D, Ramzan N. Performance analysis of an integrated fixed bed gasifier model for different biomass feedstocks. Energies 2013;6:6508–24.
[8] Block C, Ephraim A, Hortala EW, Minh DP, Nzihou A, Vandecasteele C. Co-pyrogasification of plastic and biomass, a review. Waste Biomass Valorization 2018;10(3):483–509.
[9] Chai Y, Gao N, Wang M, Wu C. H_2 production from co-pyrolysis/gasification of waste plastics and biomass under novel catalyst Ni-CaO-C. Chem Eng J 2020;382:122947.
[10] Chai Y, Wang M, Gao N, Duan Y, Li J. Experimental study on pyrolysis/gasification of biomass and plastics for H_2 production under new dual-support catalyst. Chem Eng J 2020;396:125260.
[11] Cortazar M, Sun S, Wu C, Santamaria L, Olazar L, Fernandez E, et al. Sorption enhanced ethanol steam reforming on a bifunctional Ni/CaO catalyst for H_2 production. J Environ Chem Eng 2021;9(6):106725.
[12] Cortazar M, Gao N, Quan C, Suarez MA, Lopez G, Orozco S, et al. Analysis of hydrogen production potential from waste plastics by pyrolysis and in line oxidative steam reforming. Fuel Process Technol 2022;225:107044.
[13] Deng N, Li D, Zhang Q, Zhang AW, Cai R, Zhang B. Simulation analysis of municipal solid waste pyrolysis and gasification based on Aspen plus. Frontiers in Energy 2017;13(1):64–70.
[14] Ding Y, Olumayegun O, Chai Y, Liu Y, Wang M. Simulation, energy and exergy analysis of compressed air energy storage integrated with organic Rankine cycle and single effect absorption refrigeration for trigeneration application. Fuel 2022;317:123291.
[15] EU, 2018, Directive (EU) 2018/2001 of the European Parliament and of the Council of 11 December 2018 on the promotion of the use of energy from renewable sources, OJ L 328, 21.12.2018, p. 82-209.
[16] Fernandez E, Amutio M, Artetxe M, Arregi A, Santamaria L, Lopez G, et al. Assessment of product yields and catalyst deactivation in fixed and fluidized bed reactors in the steam reforming of biomass pyrolysis volatiles. Process Saf Environ Prot 2021;145:52–62.
[17] Fernandez E, Santamaria L, Artetxe M, Amutio M, Arregi A, Lopez G, et al. Conditioning the volatile stream from biomass fast pyrolysis for the attenuation of steam reforming catalyst deactivation. Fuel 2022;312:122910.
[18] Garcia L, Salvador ML, Arauzo J, Bilbao R. CO_2 as a gasificying agent for gas production from pine sawdust at low temperatures using a Ni/Al coprecipitated catalyst. Fuel Process Technol 2001;69(2):157–74.
[19] Gerun L, Paraschiv M, Vijeu R, Bellettre J, Tazerout M, Gobel B, et al. Numericial investiogation of the partial oxidation in a two-stage downdraft gasifier. Fuel 2008;87:1383–93.
[20] Irena. Renewable Energy Prospects for the European Union. accessed on 1st July, 2021, https://www.irena.org/publications/2018/Feb/Renewable-energy-prospects-for-the-EU; 2018.
[21] Jess A. Mechanisms and kinetics of thermal reactions of aromatic hydrocarbons from pyrolysis of solid fuels. Fuel 1996;75(12):1441–8.
[22] Kannan P, Shoaibi AA, Srinivasakannan C. Process simulation and sencivity analysis of waste plastics gasification in a fluidized bed reactor. Waste Management and the Environment 2012;163:177–86.
[23] Kaushal P, Tyagi R. Advanced simulation of biomass gasificaiton in a fluidized bed reactor using Aspen Plus. Renewable Energy 2017;101:629–36.
[24] Kumar A, Jones DD, Hanna MA. Thermochemical Biomass Gasification: A review of the Current Status of the Technology. Energies 2009;2:556–81.
[25] Li J, Burra KRG, Wang Z, Liu X, Gupta AK. Co-gasification of high-density polyethylene and pretreated pine wood. Appl Energy 2021;285:116472.
[26] Lopez G, Artetxe M, Amutio M, Alvarez J, Bilbao J, Olazar M. Recent advances in the gasification of waste plastics. A critical overview, *Renewable and Sustainable Energy Reviews* 2018;82:576–96.
[27] Mohammed JK, Chowdury AA, Rasul MG. Pyrolysis of municipal green waste: A modelling, simulation and experimental analysis. Energies 2015;8:7522–41.
[28] Muratori M, Calvin K, Wise M, Kyle P, Edmonds J. Global economic consequences of deploying bioenergy with carbon capture and storage (BECCS). Environ Res Lett 2016;11(9):095004.
[29] Nikoo MB, Mahinpey N. Simulation of biomass gasification in fluidised bed reactor using ASPEN PLUS. Biomass Bioenergy 2008:1245–54.
[30] Ono Y, Fukuda Y, Sumitani Y, Mastsukawa Y, Satio Y, Matsushita Y, et al. Experimental and numerical study on degradation behaviour of coke with CO_2 or H_2O gasification reaction at high temperature. Fuel 2022;309:122061.
[31] Pauls JH, Mahinpey N, Mostafavi E. Simulation of air-steam gasification of woody biomass in a bubbling fluidized using Aspen Plus: A comprehensive model including pyrolysis, hydrodynamics and tar production. Biomass Bioenergy 2016;95:157–66.
[32] Rafati M, Hashemisohi A, Wang L, Shahbazi A. Sequential modular simulation of hydrodynamics and reaction kinetics in a biomass bubbling fluidized-bed gasifier using Aspen Plus. Energy Fuels 2015;29:8261–72.
[33] Ravenni G, Elhami OH, Ahrenfeldt J, Henriksen UB, Neubauer Y. Adsorption and decomposition of tar model compounds over the surface of gasification char and active carbon within the temperature range 250–800 °C. Appl Energy 2019;241:139–51.
[34] Song H, Yang H, Zhao C, Hu J, Zou J, Wu P, et al. Co-gasification of petroleum coke with coal at high temperature: Effects of blending ratio and the catalyst. Fuel 2022;307:121863.
[35] U.S EIA (2017), EIA projects 28% increase in world energy use by 2040, https://www.eia.gov/todayinenergy/detail.php?id=32912, accessed on 1st July,2021.
[36] Shen Y, Ma D, Ge X. CO2 – looping in biomass pyrolysis or gasification. Sustainable Energy Fuels 2017;1(8):1700–29.
[37] Wang M, Lawal A, Stephenson P, Sidders J, Ramshaw C. Post-combustion CO2 capture with chemical absorption: A state-of-the-art review. Chem Eng Res Des 2011;89(9):1609–24.
[38] Wang M, Joel AS, Ramshaw C, Eimer D, Musa N. Process intensification for post-combustion CO2 capture with chemical absorption: A critical review. Appl Energy 2015;158:275–91.
[39] Wang M, Wan Y, Guo Q, Bai Y, Yu G, Liu Y, et al. Brief review on petroleum coke and biomass/coal co-gasification: Syngas production, reactivity characteristics, and synergy behaviour. Fuel 2021;304:121517.
[40] Wong SL, Ngadi N, Abdullah TAT, Inuwa IM. Current state and future prospects of plastic waste as source of fuel: A review. Renew Sustain Energy Rev 2015;50:1167–80.
[41] Xu F, Xing X, Gao S, Zhang W, Zhu L, Wang Y, et al. Direct chemical looping gasification of pine sawdust using Fe_2O_3-rich sludge ash as an oxygen carrier: Thermal conversion characteristics, product distributions, and gasification performances. Fuel 2021;304:121499.
[42] Yao D, Hu Q, Wang D, Yang H, Wu C, Wang X, et al. Hydrogen production from biomass gasification using biochar as a catalyst/support. Bioresour Technol 2016;216:159–64.
[43] Abu El-Rub ZEB. Experimental comparison of biomass chars with other catalysts for tar reduction. Fuel 2008:2243–52.