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**Box-Behnken design based CO₂ co-gasification of horticultural waste and sewage sludge
with addition of ash from waste as catalyst**

Xiang Kan^{a,b}, Xiaoping Chen^{c,d}, Ye Shen^{a,b}, Alexei A. Lapkin^{c,e}, Markus Kraft^{c,e}, Chi-Hwa Wang^{b*}

^aNUS Environmental Research Institute, National University of Singapore, 1 Create Way, Create Tower, #15-02, Singapore 138602

^bDepartment of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117585

^cCambridge Centre for Advanced Research and Education in Singapore Ltd., 1 Create Way, CREATE Tower #05-05, Singapore, 138602, Singapore

^dSchool of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459

^eDepartment of Chemical Engineering and Biotechnology, University of Cambridge, Philippa Fawcett Drive, Cambridge CB3 0AS, United Kingdom

Corresponding author:

Chi-Hwa Wang*

Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117585, Singapore.

E-mail: chewch@nus.edu.sg

Tel: (65) 6516 5079.

Abstract

CO₂ co-gasification of horticultural waste (HW) and sewage sludge (SS) with addition of ash from waste as catalyst in a fixed-bed lab-scale gasifier was comprehensively investigated using Box-Behnken experiment design. Influence of three operating parameters, *i.e.* loaded ash content, operating temperature, and gasifying agent flow rate was studied. Among the three parameters, temperature is the main driving force for enhancement of cold gas efficiency (CGE) and higher heating value (HHV) of the produced syngas. An increase in the gasifying agent flow rate is found to positively impact CGE, but to negatively affect the HHV of the produced syngas and the CO₂ reduction ratio. The increase in ash content is observed to have a negative effect at the beginning, followed by a positive effect near the end on both CGE and HHV of the produced syngas at low temperature. Mathematical models of good accuracy, with R² 0.994 and 0.989 for CGE and HHV of the produced syngas respectively, were developed for optimization of the different indices of the co-gasification process by response surface methodology (RSM). Finally, a KIVA-CHEMKIN based CFD model was implemented to study the combustion performance of the produced syngas in an internal combustion engine (ICE). The engine efficiency is observed to be proportional to HHV of the produced syngas, while inversely proportional to its CO₂ content, which may cause engine failure when exceeds 74% v/v, in the present study.

Keywords: Horticultural waste; Sewage sludge; CO₂ gasification; Box-Behnken design; Syngas; Engine.

1. Introduction

Biomass gasification is a multi-step thermochemical conversion process. Biomass is initially pyrolyzed through evaporation and devolatilization to form carbonaceous char, and then partially oxidized to produce syngas, comprising mainly CO, H₂, CH₄, and CO₂ [1]. This demonstrates key advantage of the technology over other existing technologies of waste treatment in flexibility of utilization of the end products either through *in situ* heat/power generation, or production of liquid/gaseous chemicals, and minimizing the volume of municipal solid waste (MSW) [2, 3]. The composition of the produced syngas may vary significantly, depending largely on the operating parameters (e.g. temperature and pressure) and gasifying agent (e.g. steam, air, pure oxygen and CO₂). In addition to the merit of carbon neutrality of the biomass itself, CO₂ biomass gasification, which is one of approaches of carbon capture and utilization (CCU), incorporates CO₂ into a valorisation cycle, thus contributing to reducing in atmospheric CO₂ concentration. [4, 5].

The main combustible gaseous product of CO₂ gasification, based on Boudouard reaction ($C + CO_2 \leftrightarrow 2CO$), is CO, which offers potential pathways for direct power generation, production of hydrogen through water-gas shift reaction, and synthesis of liquid fuels via Fischer-Tropsch process in combination with H₂ or other chemicals [6, 7]. However, reactivity of the CO₂ biomass gasification is largely limited by the char gasification step, specifically Boudouard reaction, since the rate of this heterogeneous gas–solid reaction is much slower than that of other reactions involved in CO₂ gasification, such as the preliminary steps of evaporation and devolatilization [8]. Moreover, Boudouard reaction is endothermic with a large positive enthalpy (172 kJ mol⁻¹ at 25 °C), and the reaction only proceeds in forward direction to produce CO when temperature is high, typically above 700 °C, when the large positive entropic term ($T\Delta S$) prevails the enthalpic component (ΔH) and Gibbs free energy becomes negative ($\Delta G = \Delta H - T\Delta S$) [8]. To further enhance the char reaction rate, different catalytic species have been used, as reported in the existing literature [4, 9, 10]. Through addition of the alkali and alkaline earth metals (AAEMs), such as K and Ca, or transition metals, such as Fe, reactivity in the catalysed reactions increases by over an order of magnitude. This brings along the energetic benefit of lowering the gasification operating temperature, and the economic benefit of improving the throughput of the gasification facility, attributed to the catalytic effect of increasing the number of the carbon active sites on the biomass surface. For example, rice husk char supported Ni–Fe catalysts were utilized by Shen et al. [11] to enhance the tar conversion for gasification: conversion could reach about 92.3% under the

optimized conditions. Likewise, Yuan et al. [12] investigated the recovery process of potassium catalyst (K_2CO_3) in a bench-scale bubbling fluidized bed reactor by changing operating parameters of washing methods and found that the optimal recovery efficiency from the residues was 87.62%. In addition, Liu et al. [13] studied the microalgae gasification in the presence of Fe_2O_3 oxygen carrier and CaO additive in a fixed bed reactor, revealing that CaO was the key catalytic species and exhibited good selectivity to synthesis gas production at 850 °C.

Most of the current studies are focused on addition of external pure catalysts, which necessarily involves extra energetic and economic inputs for both, the catalyst preparation and its regeneration in real applications. In the present study, to avoid the use of a pure catalyst, ash from the feedstock itself, containing large proportions of AAEMs, is utilised as a catalyst. This is proposed as a more attractive and cheaper option, more suitable to the emerging paradigm of circular economy [14].

Previous studies provided substantial reference data on gasification of single MSW feedstock, while there is insufficient information on reactivity and catalytic effect of MSWs' co-gasification. Therefore, two typical MSWs, *i.e.* horticultural waste (HW) and sewage sludge (SS), with relatively high ash contents, were selected as the feedstocks for co-gasification in the present study, based on the concept of positive synergetic effect between different feedstocks [15].

The oxygen-exchange mechanism is commonly used to describe the Boudouard reaction, according to which CO_2 molecule is first dissociated at a free carbon active site on the surface of biomass char, creating a reactive surface complex of carbon–oxygen and a molecule of CO, followed by desorption process where the created carbon–oxygen species are transferred to the gas phase with the production of a new vacant carbon active site and another molecule of CO [16, 17]. Under this mechanism, the rate of catalytic gasification is significantly increased in the presence of AAEMs and transition metals in the char. This results from the increase in the number of free carbon active sites induced by the metals, which has been widely regarded as a predominant factor affecting reactivity in low rank coal and biochar gasification [18, 19]. Keiichirou et al. [9] investigated the effects of potassium and calcium on CO_2 gasification reactivity of the catalyst-loaded chars prepared by impregnation methods using solutions of K_2CO_3 and $Ca(OH)_2$, with thermal gravimetric analysis (TGA), and concluded that the presence of K and Ca compounds in char improved reactivity for CO_2 gasification. Fan et al. [4] studied the effects of $FeCO_3$ as a catalyst precursor on CO_2 gasification of a sub-bituminous Wyodak coal in a fixed-bed laboratory gasifier and detected that the apparent activation energy decreased from 92.7 to 58.3 kJ mol⁻¹

through the addition of 3 wt% Fe to the coal. Likewise, CO₂ gasification of fir char loaded with five metal catalysts (K, Na, Ca, Mg, and Fe), prepared by solutions of CH₃COOK, CH₃COONa·3H₂O, Ca(CH₃COO)₂·H₂O, Mg(CH₃COO)₂·4H₂O and Fe(NO₃)₃·9H₂O correspondingly, were conducted by Yanqin et al. [10] and it was proposed that the CO₂ gasification reactivity was upgraded by the added metals in the order of K>Na>Ca>Fe>Mg. However, to the authors' best knowledge, few studies have been conducted on the analysis of catalytic effect utilizing ash from the biomass feedstock itself on the CO₂ co-gasification. One of the advantages of co-gasification, which has been demonstrated in our previous work [20], is that gasification of sewage sludge alone may produce low-quality syngas, which may reduce throughput of the gasification facility and cause difficulties in the downstream utilisation system due to the relatively low higher heating value (HHV) of the input sludge. Furthermore, gasification of high-ash (~25wt%) sludge alone may cause agglomeration in the reactor and hinder the gasification process, as a result of the large content of SiO₂ in the sludge ash, which may form silicates with low melting point during the gasification process and melt at elevated temperatures [21], leading to the coverage of the available carbon active sites and consecutive deactivation of catalysts for gasification. In this regard, co-gasification also has the advantages of mitigating the problem of agglomeration, due to the high calcium content in the HW ash, which was reported to be able to lower the risk of agglomeration [22, 23], enhance HHV of the produced syngas, and increase and the solid-to-gas conversion efficiency [24].

The aim of the present study is to investigate the effects of ash content, temperature and flow rate of the gasifying agent on HHV of the produced syngas, CO₂ reduction efficiency, and cold gas efficiency (CGE) of the CO₂ gasification in a fixed-bed lab-scale gasifier using Box-Behnken design (BBD). In order to predict the optimized conditions under different scenarios, empirical correlations between the operating parameters and the dependant variables, namely HHV of produced syngas, CO₂ reduction and CGE, were generated using the response surface methodology (RSM). Last but not least, to make this waste-to-energy study more complete with consideration of the downstream energy utilisation, a KIVA-CHEMKIN based CFD model was implemented to study the combustion performance of the produced syngas in internal combustion

engine (ICE) with its concept presented in Fig. 1, which has rarely been covered in the existing gasification studies.

Figure 1. Schematic diagram of gasification experiment setup and concept of its integration with KIVA-CHEMKIN based engine CFD model.

2. Materials and methods

2.1 Characterization of gasification feedstock

2.1.1 Samples sources

The HW, a typical lignocellulosic MSW, was selected as a feedstock in this study, provided by NUS campus waste collection point, and was stored in a dry box at ambient temperature before use. The raw sewage sludge (SS) samples were collected from a large-scale mesophilic anaerobic digester, handling municipal waste water, after the dewatering process at Ulu Pandan Water Reclamation Plant, Singapore. The wet SS samples were sealed and kept in a cold room with ambient temperature around 4 °C before use.

2.1.2 TGA, CHNS, ICP and XRD analysis

The HW ash (HWA) and SS ash (SSA) were prepared through placing the raw HW and SS samples in a muffle furnace at a constant temperature of 800 °C for 4 h. Ash samples were stored in a dry box before use. All samples were pre-dried in a convection oven at 105 °C and ground into fine powders using a ball mill (Tencan Powder XQM-2-12, China) to have a homogeneous mixture, as the representative samples for TGA (Discovery TGA, USA), CHNS (Elementar vario MICRO cube, Germany) and ICP (Perkin Elmer Optima 5300DV, USA) analysis. The HHV of the solid biomass waste was calculated using Eq. (1) [25],

$$HHV_s = (\%TS_s) \times [0.3708(\%C) + 1.1124(\%H) - 0.1391(\%O) + 0.3178(\%N) + 0.1391(\%S)]/100 \quad (1)$$

where HHV_s is the HHV of the input solid biomass waste at standard state; $(\%C)$, $(\%H)$, $(\%O)$, $(\%N)$, $(\%S)$ is the elemental mass percentage of the oven-dried sample and $(TS\%)$ is the total solids' mass percentage of the raw sample. The limitation of this equation is that it neglects the inorganic carbon, hence it might not be accurate when there is a significant concentration of inorganic carbon in the waste feed.

2.2 Sample preparation and gasification experiment design

2.2.1 Sample preparation

All the samples, *i.e.* HW, SS, HWA and SSA, were oven-dried, ball milled, and sieved to achieve a homogenous distribution of particle sizes before experiment. The powder samples of HW and SS were mixed in a ratio of 1:4 based on findings from our previous work [20, 26]. Subsequently, certain amounts of mixed ash samples (20 wt% SSA) of HWA and SSA were added to the biomass samples, *i.e.* mixed powder samples (20 wt% SS) of HW and SS, and well stirred according to the loaded ash content of the experiment design shown in Table 1. Afterwards, the powder mixtures were added into a metal mould with a pore diameter of 3 mm and height of 4 mm. Subsequently, the metal mould was subjected to a constant pressure of 4 bar using a hydraulic machine for 5 mins to pelletize the powder mixtures as feedstock for the gasification experiment.

2.2.2 Gasification experiment setup

The gasification experiment setup used in the present study is shown in Fig. 1. The gasifying agent was fed by two mass flow controllers (Sevenstar CS200, China) producing a mixture of 20 vol% CO_2 and 80 vol% N_2 of which nitrogen served as internal standard ranging between 48 and 80 mL(STP) min^{-1} . The furnace (Carbolite-MTF12/25/400, UK) was well insulated, using materials with low thermal mass on its surface to provide better efficiency, and integrated with a temperature controller. The pelletized feedstocks were placed in the middle of the stainless-steel tube reactor, with an inner diameter of 3.3 mm and length of 60 cm, close to the thermocouple of the temperature controlling system for a better accuracy of monitoring the reaction temperature. After loading the gasification feedstocks, for each experiment run, the furnace was heated up from ambient temperature, around 25 °C, to the highest temperature of the experiment, given in Table 1, at a

constant heating rate of 50 °C min⁻¹ and kept at that temperature till the end of the experiment. When temperature inside the reactor reached 100 °C, the gas sampling bag was connected at the end of the apparatus for continuous sampling over 40 mins. The produced syngas was first filtered by the organic solvent to remove tar content, before being charged to the sampling bag for gas composition analysis using gas chromatograph (PerkinElmer Clarus 580 GC, USA) equipped with a thermal conductivity detector. After gas sampling, the furnace was shut down and the gasifying agent was switched to pure nitrogen at a flow rate of 80 mL(STP) min⁻¹ for cooling purpose. Lastly, once the furnace temperature had reached ambient, the produced biochar was collected and sealed for further analysis.

2.2.3 BBD of the gasification experiment

In the present study, impacts of three most significant parameters, ash content of 5-25 wt%, temperature of 700-900 °C, and gasifying agent flow rate of 60-100 mL min⁻¹, were investigated, through employing the BBD and RSM, on the responses, *e.g.* HHV of produced syngas, CO₂ reduction and CGE. BBD is an independent, rotatable quadratic design, where the variable combinations are at the midpoints of the edges and the centre of the variables space [27, 28]. The loaded ash content was defined as the ratio of the weight of the added ash samples (mixture of HWA and SSA) to the total weight of the feedstocks. To guarantee data reproducibility and accuracy of the developed statistical model, run 13, the centre run of BBD, was conducted in duplicate. Also, since the key interest of the present study is the catalytic effect of added ash on CO₂ co-gasification, runs 14 and 15, with ash content of 10 and 20 wt% respectively, were inserted into the original BBD for a more precise monitoring of the effect of ash content. Additionally, experiment results of run 16 were used as verification data for the developed mathematic models, which were excluded when generating the statistical models. The complete BBD of gasification operating parameters is shown in Table 1.

Table 1. Box–Behnken design of gasification operating parameters.

Run No.	Ash content (A, wt%)	Temperature (T, °C)	Gasifying agent flow rate (F, mL min ⁻¹)	Biomass sample ^d (mg)	Ash sample (mg)	Feedstock (mg)
1	5(-1) ^a	700(-1)	80(0)	511	27	538
2	5(-1)	900(1)	80(0)	516	27	543
3	25(1)	700(-1)	80(0)	515	172	687
4	25(1)	900(1)	80(0)	514	171	685
5	5(-1)	800(0)	60(-1)	504	27	531

6	5(-1)	800(0)	100(1)	504	27	531
7	25(1)	800(0)	60(-1)	512	171	683
8	25(1)	800(0)	100(1)	512	171	683
9	15(0)	700(-1)	60(-1)	507	89	596
10	15(0)	700(-1)	100(1)	500	88	588
11	15(0)	900(1)	60(-1)	501	88	589
12	15(0)	900(1)	100(1)	503	89	592
13	15(0)	800(0)	80(0)	505	89	594
14 ^b	10(-0.5)	800(0)	80(0)	502	56	558
15 ^b	20(0.5)	800(0)	80(0)	504	126	630
16 ^c	0(-1.5)	800(0)	80(0)	511	0	511

^a The coded values of Box-Behnken design are presented in brackets.

^b Run 14 and 15 were added to the original Box-Behnken design for precise monitoring of ash content effect.

^c Experiment results of run 16 were used as verification for the developed mathematic models.

^d Biomass sample was a mixture of 80 wt% dry HW sample and 20 wt% dry SS sample.

2.3 Analytical methods

Second-order polynomial model of RSM is widely used for parametric studies based on experimental results generated from BBD [28, 29]. In this work, second-order polynomial equations with three variables. *i.e.* ash content (A), temperature (T), and gasifying agent flow rate (F), were applied to fit the responses, *e.g.* HHV of produced syngas, CO₂ reduction and CGE, for different experiment runs, with the most insignificant lack of fit and the largest adjustment coefficient of determination [30]. The HHV of produced syngas, CGE and CO₂ reduction focused in the present study are defined as shown in Eqs. (2) - (4),

$$HHV_{g,syn} = \frac{\sum HHV_k \times (vol\% gas_k)}{100} \quad (2)$$

$$CGE = \frac{HHV_{g,syn} \times n_{g,syn} \times 0.0224}{HHV_{s,ga} \times m_{s,ga}} \quad (3)$$

$$CO_2 \text{ reduction}(\%) = \frac{F \times y_{CO_2} \times t - V_{CO_2,eff}}{F \times y_{CO_2} \times t} \times 100(\%) \quad (4)$$

where $HHV_{g,syn}$ is the average HHV of the produced syngas; HHV_k is the HHV of gas component k at standard state [31]; $vol\% gas_k$ is the volumetric percentage of gas component k; $n_{g,syn}$ is the total moles of produced syngas; $HHV_{s,ga}$ is the HHV of the feedstocks for gasification; $m_{s,ga}$ is the total weight of the feedstocks consumed during the CO₂ gasification process; F is the gasifying agent flow rate; y_{CO_2} is the molar ratio of CO₂ in the gasifying agent, 0.2; t is the gas sampling

time, 40 mins; $V_{CO_2,eff}$ is the total volume of the CO_2 in the effluent collected in the gas sampling bag.

The mathematical models developed via RSM have a quadratic form as shown in Eq. (5),

$$Y_i = \alpha_0 + \alpha_1 A + \alpha_2 T + \alpha_3 F + \alpha_{11} A^2 + \alpha_{22} T^2 + \alpha_{33} F^2 + \alpha_{12} AT + \alpha_{13} AF + \alpha_{23} TF \quad (5)$$

where Y_i (*e.g.* $Y_{HHV_{g,syn}}$, Y_{CGE} and $Y_{CO_2 \text{ reduction}}$) is the predicted response; A is mass percentage of the ash content loaded into the gasification feedstock; T is the highest temperature; F is the gasifying agent flow rate; α_0 is a constant; α_1 , α_2 and α_3 are the linear coefficients; α_{11} , α_{22} and α_{33} are the quadratic coefficients; α_{12} , α_{13} and α_{23} are the cross-coefficients. The adequacy of the developed model was further checked against the experiment result of run 16 together with the analysis of variance (ANOVA) method.

The optimization was conducted using different success indicators mentioned above and defined in Eq. (6).

$$\max_{A,T,F} Y_i(A,T,F) \text{ such that } \begin{cases} 5 \leq A \leq 25 \\ 700 \leq T \leq 900 \\ 60 \leq F \leq 100 \end{cases} \quad (6)$$

Although the RSM adopted in the present study has been proven to have its merits of well-fitting to nonlinear dynamical data and easy implementation in cases with restricted data points, the model developed via RSM still has its limitation in situations where the operating parameters are out of the screened range, owing to its empirical nature, *e.g.* application in estimation of gasification with other biomass inputs or cases with much lower gasifying agent flow rates than the current work [28]. However, analysis methods established in this work can be easily employed to gasification cases with other biomass inputs and different operating conditions.

2.4 Engine CFD model

Most of the existing studies on CO_2 gasification focused mainly on trying to enhance either the reactivity or the CGE of the gasification process, whereas neglecting the dilution effect of the CO_2 in the produced syngas, which may cause severe problems for the downstream utilization systems, like ICE. Therefore, in the present study, an advanced CFD modelling code developed by Los Alamos National Laboratory (LANL) [32], KIVA4, was coupled with a chemical kinetics solver, CHEMKIN, to simulate the fluid flow and chemical reactions inside the combustion chamber of the ICE fuelled by the produced syngas from CO_2 gasification. Since the original KIVA4 only takes into account 12 active chemical species in the reaction chemistry, in order to have a more

accurate prediction of syngas combustion in ICE, a more detailed reaction mechanism, GRI-Mech 3.0, considering related chemical kinetics and fuel properties of syngas was integrated through CHEMKIN. GRI-Mech 3.0 reaction mechanism, containing 53 species and 325 reactions, is an optimized mechanism for syngas oxidation simulation, comprised of a list of elementary chemical reactions and the associated rate constant expressions [33]. It has been experimentally confirmed and widely employed in the existing literature [34, 35]. In the present study, it was used as an input file in the CHEMKIN code to solve the chemical kinetics of syngas combustion. Other main advantages of utilising this integrated KIVA-CHEMKIN based CFD model are: saving experimental cost and predicting detailed interacting phenomena between the species during combustion, which may not be easily acquired from experiments [36].

In the proposed KIVA-CHEMKIN framework, for each time step, KIVA4 provides initial conditions of all the species in each computational cell to CHEMKIN for reaction calculation. Afterwards, the updated conditions of all the species are sent back to KIVA4 for heat and mass transfer calculation between the computational cells, where the convective and diffusive transports are simulated according to the RNG k- ϵ turbulence model. Regarding the simulation of spark ignition process, additional energy determined by experimental data is added to the internal energy of a block of cells surrounding the spark plug location, predefined as spark cells, on each time step during the spark ignition process. Conservation equations of mass, momentum and energy are solved in KIVA4 according to Eqs. (7)-(9).

Conservation of mass for species m ,

$$\frac{\partial \rho_m}{\partial t} + \nabla \cdot (\rho_m u) = \nabla \cdot \left(\rho D \nabla \left(\frac{\rho_m}{\rho} \right) \right) + \dot{\rho}_m^C \quad (7)$$

where ρ_m is the density of species m ; u is the fluid velocity vector; ρ is the density of total mass; D is the single diffusion coefficient with the assumption of Fick's law and estimated using kinematic viscosity and Schmidt number [37]; $\dot{\rho}_m^C$ is the chemical source term contributed by chemical reactions.

Conservation of momentum,

$$\frac{\partial (\rho u)}{\partial t} + \nabla \cdot (\rho u u) = \rho g - \frac{1}{a^2} \nabla p + \nabla \cdot \sigma - A_0 \nabla \cdot \left(\frac{2}{3} \rho k \right) \quad (8)$$

where g is the specific body force; a is the dimensionless quantity used together with the pressure gradient scaling method to enhance computational efficiency in low Mach number flows; p is the

pressure of the fluid; σ is viscous stress tensor; A_0 is set to unity when employing turbulence models; k is the turbulent kinetic energy.

Conservation of energy,

$$\frac{\partial(\rho I)}{\partial t} + \nabla \cdot (\rho u I) = -\nabla \cdot J + (1 - A_0)\sigma : \nabla u + A_0 \rho \varepsilon + \dot{Q}^C - p \nabla \cdot u \quad (9)$$

where I is specific internal energy, not including chemical energy; J is the heat flux vector contributes by both enthalpy diffusion and heat conduction; ε is dissipation rate of the turbulent; $\dot{Q}^C$ is the chemical source term related to chemical heat release.

The structure information of a 4-stroke, 4-cylinder, and naturally aspirated SI engine (VovacPower VF4100P, China) was used to generate the mesh (a 60° sector mesh including 21,150 hexahedron cells) for the present simulation study. Also verification of the developed KIVA-CHEMKIN model against the experiment data was illustrated in detail in our previous work [33].

3. Results and discussion

3.1 Characterisation of the feedstocks

The results of the proximate and elemental analysis, and HHV of all the samples, *i.e.* HW, SS, HWA and SSA, are shown in Table 2. In order to identify the major compounds in the HWA and SSA, XRD analysis was conducted and it was found that the major compounds in HWA and SSA were calcite and quartz respectively, as shown in Fig. 2. This knowledge can be used to further demonstrate the benefit of co-gasification of HW and SS, since high calcium content in HW ash can lower the risk of forming silicates with a low melting point, which may lead to agglomeration during high-temperature gasification. Furthermore, at high temperatures, typically above 800 °C, calcite undergoes decomposition to produce calcium oxide, which is known to be a good CO₂ and H₂S adsorbent [2, 24]. This may potentially increase the rate of Boudouard reaction and energy recovery potential of the produced gas.

Table 2. Characterization of gasification feedstocks (HW, SS and ashes).

Samples	HW	SS	HWA	SSA
TS ^a (wt %)	84.82(±0.01)	16.12(±0.54)	-	-
VS ^a (wt %)	76.80(±0.01)	11.66(±0.40)	-	-
C ^b (wt%)	46.39(±0.16)	36.55(±0.43)	7.78(±0.00)	<0.5

H ^b (wt%)	5.57(±0.10)	5.37(±0.10)	<0.5	<0.5
N ^b (wt%)	0.97(±0.01)	6.21(±0.34)	ND	ND
S ^b (wt%)	ND	2.10(±0.00)	0.63(±0.01)	2.51(±0.04)
K ^b (wt%)	0.47(±0.00)	0.20(±0.00)	3.87(±0.04)	0.76(±0.00)
Ca ^b (wt%)	3.86(±0.02)	2.37(±0.03)	32.01(±0.97)	8.10(±0.03)
Na ^b (wt%)	0.03(±0.00)	0.10(±0.00)	0.14(±0.01)	0.38(±0.01)
Mg ^b (wt%)	0.28(±0.00)	0.44(±0.01)	2.49(±0.05)	1.58(±0.03)
Fe ^b (wt%)	0.03(±0.00)	2.38(±0.00)	0.19(±0.01)	8.25(±0.12)
Ash ^b (wt%)	8.94(±0.01)	26.58(±0.01)	-	-
HHV (MJ kg ⁻¹)	15.60(±0.11)	3.00(±0.04)	-	-

^a Values calculated based on wet samples.

^b Values calculated based on oven-dried samples.

Figure 2. XRD analysis of HWA and SSA: (a) HWA; (b) SSA.

3.2 Regression models

By means of RSM, the regression models for CGE, HHV of the produced syngas and CO₂ reduction were developed based on the experimental data from runs 1 to 15 using the format of Eq. (5). Coefficients of the different terms in the developed regression models are tabulated in

Table 3. The experimental results of syngas composition, HHV of the produced syngas and CGE for all runs are shown in Fig. 3. Among all experiment runs, run 4 shows the highest CO content, HHV of the produced syngas and CGE, which resulted from its high ash content, *i.e.* 25 wt%, and high reaction temperature, *i.e.* 900 °C. Conversely, run 1, where both ash content, *i.e.* 5 wt%, and the reaction temperature, *i.e.* 700 °C, are low, has the lowest CGE. The observed and the predicted values show good agreement with each other as shown in Figs. 4(d) and 5(d), and the errors are listed in Table 4. For instance, for run 7, the observed values for CGE, HHV of the produced syngas and CO₂ reduction are 0.298, 4.34 MJ Nm⁻³ and 8.16%, compared to the predicted values of 0.299, 4.38 MJ Nm⁻³ and 8.89%, with absolute errors of 0.001, 0.04 MJ Nm⁻³ and 0.74% respectively. Additionally, since the experimental data for run 16 were excluded for the development of the regression models, they can be used separately as verification data. For run 16, the observed values for CGE, HHV of produced syngas and CO₂ reduction are 0.257, 3.16 MJ Nm⁻³ and 8.56%, compared to the predicted values of 0.239, 3.16 MJ Nm⁻³ and 9.49%, with absolute errors of 0.018, 0.00 MJ Nm⁻³ and 0.93% respectively, successfully demonstrating accuracy of the developed regression models.

Table 3. Coefficients for syngas HHV, CGE and CO₂ reduction regression models.

Terms	Coefficients		
	Syngas HHV	CGE	CO ₂ reduction
Constant	2.55E+01	4.73E+00	2.01E+02
A	-1.34E-01	-1.62E-02	-2.35E+00
T	-7.05E-02	-1.17E-02	-6.90E-01
F	-4.54E-02	-1.68E-02	1.31E+00
A*T	7.23E-05	1.31E-05	1.68E-03
A*F	-3.92E-04	-1.44E-05	4.26E-03
T*F	-5.23E-05	1.45E-05	-1.45E-03
A ²	5.13E-03	3.73E-04	2.88E-02
T ²	5.98E-05	7.84E-06	5.55E-04
F ²	4.39E-04	4.01E-05	-1.14E-03

Accuracy of these models is further confirmed by ANOVA method. An example of ANOVA for CGE regression model is shown in Table 5. Significance of the CGE model is confirmed by the small p-value of the derived model, 4.99E-07, signifying that almost all variance caused by altering the operating condition can be captured by this second-order polynomial model. Furthermore, based on the derived regression models, the optimized operating conditions for the highest CGE, HHV of produced syngas and CO₂ reduction according to Eq. (6), are (A: 25 wt%, T: 900 °C, F: 100 mL min⁻¹), (A: 25 wt%, T: 900 °C, F: 60 mL min⁻¹) and (A: 25 wt%, T: 900 °C, F: 60 mL min⁻¹) respectively.

Figure 3. Syngas composition, HHV of produced syngas and CGE for different experiment runs.

In conclusion, through comparison between the predicted and the observed results and the ANOVA study, the developed regression models for CGE and HHV of the produced syngas show good accuracy, with the square of correlation coefficients ($R^2 = \text{Sum of squares (Model)} / \text{Sum of squares (Total)}$) equal to 0.994 and 0.989 respectively, indicating that the developed models can cover 99% of the total variations with good reliability.

Table 4. The observed and statistical model predicted values of syngas HHV, CGE and CO₂ reduction.

Run No.	Syngas HHV (MJ Nm ⁻³)			CGE			CO ₂ reduction (%)		
	Observed	Predicted	Error	Observed	Predicted	Error×10 ³	Observed	Predicted	Error
1	1.05	1.22	0.16	0.08	0.08	5.30	-2.09	3.32	5.41
2	5.62	5.48	-0.13	0.50	0.50	-3.20	24.60	21.60	-2.97
3	1.90	1.99	0.09	0.14	0.14	-0.16	1.22	3.99	2.76
4	6.75	6.55	-0.20	0.62	0.61	-8.66	34.60	29.00	-5.62
5	3.37	3.31	-0.06	0.22	0.21	-7.82	8.32	6.57	-1.75
6	2.63	2.55	-0.08	0.26	0.25	-3.53	7.27	6.32	-0.95
7	4.34	4.38	0.04	0.30	0.30	0.17	8.16	8.89	0.74
8	3.29	3.31	0.02	0.33	0.33	4.46	10.50	12.10	1.54
9	1.75	1.62	-0.14	0.10	0.10	-0.42	0.39	-3.30	-3.69
10	1.03	0.91	-0.12	0.09	0.08	-4.72	8.44	3.95	-4.49
11	6.08	6.24	0.16	0.48	0.49	8.08	19.40	24.10	4.70
12	4.94	5.12	0.18	0.58	0.58	3.78	15.90	19.80	3.89
13	2.88	2.70	-0.19	0.24	0.22	-15.70	7.01	6.04	-0.97
14	2.22	2.60	0.38	0.18	0.21	32.00	4.41	5.75	1.34
15	2.80	3.06	0.26	0.23	0.25	21.80	5.77	7.77	1.99
16	3.16	3.16	0.00	0.26	0.24	-18.70	8.56	9.49	0.93

Table 5. ANOVA of the regression model for the prediction of CGE.

Source	Sum of squares	Degree of freedom	Mean square ^b	F value ^c	p-Value ^d
A	1.55E-02	1	1.55E-02	4.27E+01	3.23E-04
T	3.92E-01	1	3.92E-01	1.08E+03	6.29E-09
F	2.98E-03	1	2.98E-03	8.20E+00	2.42E-02
A*T	6.83E-04	1	6.83E-04	1.88E+00	2.13E-01
A*F	3.33E-05	1	3.33E-05	9.17E-02	7.71E-01
T*F	3.35E-03	1	3.35E-03	9.22E+00	1.89E-02
A ²	5.38E-03	1	5.38E-03	1.48E+01	6.30E-03
T ²	2.59E-02	1	2.59E-02	7.14E+01	6.42E-05
F ²	1.08E-03	1	1.08E-03	2.98E+00	1.28E-01
Model	4.47E-01	9	4.97E-02	1.37E+02	4.99E-07
Residual	2.54E-03	7	3.63E-04		
Total ^a	4.50E-01	16			

^a Sum of squares (Total) = Sum of squares (Model) + Sum of squares (Residual)

^b Mean square= Sum of squares / Degree of freedom

^c F value= Mean square(Model) / Mean square(Residual)

^d p-Value means the probability when the value is bigger than F value.

3.3 Effects of operating parameters on CGE and HHV of produced syngas

3.3.1 Effect of ash content

Regarding the effect of ash content on CGE and HHV of the produced syngas, from Figs. 4(a) and 5(a), it can be seen that at low temperature, with the increase of the ash content in the feedstock, the CGE and HHV of syngas slightly decrease at the beginning; further increase in ash content leads to a continuous increase of both CGE and HHV. For instance, at 700 °C, with the increase of ash content from 5 to 12 wt%, CGE (at constant gasifying agent flow rate of 100 mL min⁻¹) and HHV (at constant gasifying agent flow rate of 60 mL min⁻¹) drop from 0.093 to 0.078 and 1.66 to 1.52 MJ Nm⁻³ respectively. A further increase of the ash content to 25 wt%, results in CGE increasing to 0.147 and HHV increasing to 2.60 MJ Nm⁻³. Similar profiles of CGE and HHV against ash content are observed under various gasifying agent flow rates, as shown in Figs. 4(b) and 5(b).

Figure 4. Response surface for the effects of ash content, temperature and gasifying agent flow rate on CGE: (a) at constant gasifying agent flow rate, 100 mL min⁻¹; (b) at constant temperature, 900 °C; (c) at constant ash content, 25 wt%; (d) predicted vs. observed plot.

However, at high temperature, the trends for both CGE and HHV at the beginning are not that clear, compared to the low-temperature conditions, showing a general increase trend in the specific

range of ash content (5-25 wt%). Specifically, at 900 °C, with the increase in ash content from 5 to 25 wt%, both CGE (at constant gasifying agent flow rate of 100 mL min⁻¹) and HHV (at constant gasifying agent flow rate of 60 mL min⁻¹) increase from 0.57 to 0.67 and 6.14 to 7.36 MJ Nm⁻³ respectively. It can be explained that the AAEMs in the ash act as catalysts for both pyrolysis and gasification steps. At high temperature, the main reaction, gasification, is largely enhanced due to catalytic effect on the increase in the number of active carbon sites on the biochar surface, resulting in an increase in both CGE and HHV. At low temperature, the main reaction is pyrolysis, the AAEMs act as catalysts to enhance the char production and CO₂ production during pyrolysis [38], thus leading to a decrease in both CGE and HHV. More details of the ash content effect on char production and CO₂ reduction will be discussed in the following section.

Figure 5. Response surface for the effects of ash content, temperature and gasifying agent flow rate on HHV of produced syngas: (a) at constant gasifying agent flow rate, 60 mL min⁻¹; (b) at constant temperature, 900 °C; (c) at constant ash content, 25 wt%; (d) predicted vs. observed plot.

3.3.2 Effect of temperature

Based on data in Table 5 and comparing the p-values of the different terms we note that two terms, namely including T and T², have the smallest p-values. This indicates that temperature is a more significant parameter affecting the dependent variable, CGE, compared to the other two observed

parameters, *i.e.* ash content and the gasifying agent flow rate. In addition, the term T^2 has a positive coefficient for all the derived regression models, as shown in Table 3, indicating that the increase in temperature during CO_2 gasification can significantly enhance HHV of the produced syngas, CGE and CO_2 reduction. According to Fig. 4(a)(c) and Fig. 5(a)(c), under all the observed conditions both, CGE and HHV of the produced syngas increase with the increase in temperature. For example, from Fig. 4(a), at the loading of ash content of 15 wt%, with the increase in temperature from 700 to 900 °C, the CGE (at constant gasifying agent flow rate of 100 mL min⁻¹) increases from 0.08 to 0.58. Besides, from Fig. 5(c), at gasifying agent flow rate of 80 mL min⁻¹, with the increase in temperature from 700 to 900 °C, the HHV (at constant ash content of 25 wt%) of the produced syngas increases from 1.99 to 6.55 MJ Nm⁻³. The explanation for this observation could be that the main reaction of CO_2 gasification, Boudouard reaction, is an endothermic reaction and the increase in temperature plays a positive effect on CO_2 reduction and favours CO formation. As temperature increases, the large positive entropic term ($T\Delta S$) prevails over the enthalpic component (ΔH), making Gibbs free energy negative ($\Delta G = \Delta H - T\Delta S$), and the reaction proceeds more favourably in the forward direction. Consequently, reactivity of the biochar is enhanced, leading to the increase of both CGE and HHV of the produced syngas.

3.3.3 Effect of gasifying agent flow rate

As regards to the effect of the gasifying agent flow rate on CGE, we observe from Fig. 4(b) that its increase has a positive effect on CGE at high temperatures. To be more specific, at the loading of as of 15 wt%, with the increase of the gasifying agent flow rate from 60 to 100 mL min⁻¹, CGE (at constant temperature of 900 °C) increases from 0.49 to 0.58. This could be verified from Knudsen diffusion theory as shown in Eqs. (10)-(11):

$$N_k = \frac{l}{d_{pore}} \quad (10)$$

$$l = \frac{3.2\mu_{\text{CO}_2}}{P} \left(\frac{RT}{2\pi MW_{\text{CO}_2}} \right)^{0.5} \quad (11)$$

where N_k and l are the Knudsen number and molecular free path of CO_2 ; d_{pore} is the pore diameter; μ_{CO_2} is the dynamic viscosity of CO_2 ; P is total pressure; R is the universal gas constant; T is temperature of the biochar particle; MW_{CO_2} is the molecular weight of CO_2 . At high temperatures, when Knudsen number (N_k) is greater than 10 [39], meaning that the mean free path of CO_2 at this condition is comparatively larger than the mean pore diameter of the

particle, the importance of pore diffusion limitation overweighs the intrinsic gasification rate as shown further in Eq. (13) and becomes the dominant factor that controls the overall gasification rate. As such, the increase of the gasifying agent flow rate causes the increase in partial pressure of CO₂ inside the reactor, enhancing diffusion of CO₂ to biochar surface, thus leading to the increase in the overall reaction rate. Moreover, it was previously reported that higher pressure suppressed volatilization and loss of mineral content and positively influenced the CO₂ gasification rate [40]. Another possible explanation could be that an increase in the gasifying agent flow rate reduces residence time of the product gas, CO, thus leading to the decrease in CO concentration inside the reactor, which lowers the inhibition effect induced by CO and shifts the equilibrium of Boudouard reaction in the forward direction [41].

However, the effect of the gasifying agent flow rate at low temperatures is not as significant as compared to that at high temperatures, Fig. 4(c). For instance, at 740 °C, an increase of the gasifying agent flow rate from 60 to 100 mL min⁻¹, has no impact on CGE (at constant ash content of 25 wt%) which remains almost unchanged around 0.20. It can be speculated that at low temperatures the chemical reaction rate is mainly under chemical control regime, not the diffusion control regime [42], meaning that regardless of the CO₂ concentration above the biochar surface, there are no vacant carbon active sites available for CO₂ adsorption. Specifically, under the chemical control regime, the desorption rate of the carbon–oxygen adsorbed species to the gas phase is relatively slow as compared to the diffusion rate of CO₂, thus leading to slow production of new vacant carbon active sites for CO₂ adsorption. This could be further explained through the widely used model for prediction of the char conversion rate [39] as shown in Eqs. (12)-(13):

$$\frac{dx}{dt} = K(1 - x)\sqrt{1 - \psi \ln(1 - x)} \quad (12)$$

$$K = k \exp\left(\frac{-E}{RT}\right) P Y_{CO_2,s}^n \quad (13)$$

where x is the char conversion; t is reaction time; K is rate constant; ψ is structural parameter; k , n and E are the pre-exponential factor, reaction order and activation energy of the Boudouard reaction, respectively; $Y_{CO_2,s}$ is the CO₂ mole fraction on particle surface. From Eq. (13), the intrinsic gasification rate predominantly depends on two parameters, *i.e.* particle surface temperature and mole fraction of CO₂ available on the particle surface. At a low T_p , the rate constant (K) is small and the intrinsic rate is lower than the diffusion rate, indicating that CO₂ can relatively easily diffuse inside the pores to drive the Boudouard reaction and

thus making the intrinsic reaction the limiting step. Therefore, the increase in mass transport cannot affect the overall chemical reaction rate, known as the intrinsic reactivity.

Unlike the effects of ash content and temperature, for which CGE and HHV share a similar profile, the effect of the gasifying agent flow rate on HHV is quite different from CGE, showing an opposite trend against each other. From Figs. 5(b)(c), with the increase in the gasifying agent flow rate, HHV of the produced syngas declines, attributed to dilution effect contributed by CO₂ in the produced syngas.

To summarize, among the three parameters, the increase in temperature acts as the main driving force in the observed range for the enhancements of char reactivity, *i.e.* CGE and HHV of the produced syngas, justified by the smallest p-value of the terms T and T² of the developed models. In contrast, the increase of ash content is found to have a negative effect at the beginning and a positive effect near the end on both CGE and HHV of the produced syngas at low temperature, while a nearly continuous positive effect at high temperature, attributed to the requirement of high temperature to trigger CO₂ gasification with ash acting as a catalyst. Finally, the increase of the gasifying agent flow rate is found to positively impact CGE, which results from the improved diffusion of CO₂ to carbon active sites and reduced CO inhibition, in contrast to its negative impact on HHV due to the dilution effect contributed by CO₂.

3.4 Analysis on CO₂ reduction and produced char

3.4.1 CO₂ reduction

As previously mentioned, the optimized operating condition for the highest CO₂ reduction ratio is A: 25 wt%, T: 900 °C and F: 60 mL min⁻¹, because high ash content and high temperature promote char reactivity and enhance the Boudouard reaction, whereas high flow rate of CO₂ may decrease the reduction ratio due to its low residence time inside the reactor, leading to a low CO₂ conversion. From Table 4, the observed CO₂ reduction of run 1 is a negative value, *i.e.* -2.09%, indicating that during the thermal process there is extra CO₂ produced, though the preferred pathway, Boudouard reaction, is a CO₂ adsorption process. It can be hypothesized that, under the operating condition of run 1, *i.e.* A: 5 wt%, T: 700 °C and F: 80 mL min⁻¹, the main reaction inside the reactor at low temperature with low ash content is the pyrolysis step, instead of gasification, and the extra CO₂ produced is one of the non-condensable gas (NCG) products from pyrolysis. Also, it has been reported by many researchers [38, 43] that the presence of metal catalysts during pyrolysis favours

oxygen removal via decarbonylation (CO rejection), decarboxylation (CO₂ rejection) and dehydration (H₂O formation) reactions, especially for the decarboxylation (CO₂ rejection) process. On the contrary, the largest CO₂ reduction, 34.60%, is observed for run 4 with operating condition of A: 25 wt%, T: 900 °C and F: 80 mL min⁻¹, because gasification takes place inside the reactor and char reactivity is largely enhanced at high temperature with high ash content.

3.4.2 Characteristics of the produced char

The findings about the trend of the char-to-feed ratio against the increase of ash content are mostly consistent with these about the effects of ash content on CGE discussed previously, meaning that when the gas yield/CGE increases, the char yield, in terms of energy proportion, generally decreases. For example, from Fig. 6, through comparison of char-to-feed ratios of runs 13, 14, 15 and 16, which share the same operating condition of temperature and the gasifying agent flow rate with the only difference in loaded ash content, one can observe that with the increase in the loaded ash content from 0 to 10 wt%, the char-to-feed ratio increases from 0.28 to 0.42 and CGE decreases from 0.26 to 0.18. A further increase in ash content to 20 wt%, results in the char-to-feed ratio dropping to 0.39 and CGE increasing to 0.23. Moreover, among all the experiment runs, run 4 and 12 have the smallest char-to-feed ratios, 0.10 and 0.07 respectively, corresponding to their largest CGEs, 0.62 and 0.58 respectively. Similar to the explanation made earlier, at the low ash content, the main reaction inside the reactor is pyrolysis and the increase in the ash content at the beginning largely enhances pyrolysis, thus resulting in the enhanced yield of char. It has previously been reported that char yield is enhanced during pyrolysis in the presence of added ash [38]. Conversely, a further increase in ash content will initiate the gasification step and cause the increase in conversion of char to gas products, thus leading to the increase in CGE and the reduction in char-to-feed ratio, resulting from the catalytic effect of the loaded ash on the gasification step.

However, HHV values of the produced char for the runs 13, 14, 15 and 16 generally follow a decreasing trend, from 17.04 to 10.55 MJ kg⁻¹, with the increase of ash content from 0 to 20 wt%. The cause of this decreasing trend is that the loaded ash content in the feedstock remains in the produced char after gasification, leading to the reduction in HHV of the produced char. More specifically, the ash contents in the produced char for the runs 16, 14, 13 and 15 are 41.30, 42.71, 49.66 and 53.82 wt% respectively, corresponding to HHV of 17.04, 14.05, 11.84 and 10.55 MJ kg⁻¹ respectively.

To sum up, high ash content and elevated temperature promote the CO₂ reduction ratio, whereas high flow rate may decrease the CO₂ reduction ratio, due to its low conversion as a result of short residence time. Additionally, regarding the char production, the increase in the ash content is found to raise the char yield at the beginning, yet followed by a decreasing trend, since high ash content may trigger gasification, when conversion of carbon to gas phase products occurs at the same temperature because of the catalytic effect of ash.

Figure 6. Char composition, char-to-feed ratio and HHV of the produced char for different experiment runs.

3.5 Engine combustion and the overall process performance

Fig. 7 illustrates engine efficiency, overall efficiency and highest temperature during syngas combustion (average temperature of the cells inside the combustion chamber) for different experiment runs. For all the observed cases, ignition timings varying between -58 to -2 CAD ATDC were investigated and the maximum brake torque (MBT) ignition timing at wide open throttle (WOT) condition was selected for comparison between the cases. The engine efficiency is found to be generally proportional to HHV and CO content of the produced syngas, while inversely proportional to CO₂ content. As shown in Fig. 7, runs 4, 11 and 2 have the largest engine efficiencies among all the experiment runs, with the values of 0.37, 0.30 and 0.24 respectively,

corresponding to their highest CO contents in the produced syngas as shown in Fig. 3, with the values of 47.03, 42.12 and 39.39 vol% respectively. The reason for the reduction in the engine efficiency could be explained as follows. The increase in CO₂ content in the input syngas fuel results in a decrease in combustion temperature inside the combustion chamber, thus leading to the decrease in thermal efficiency. From Fig. 7, it is also observed that the experimental runs, *i.e.* runs 4, 11 and 2, having the largest engine efficiencies, also possess the largest highest temperatures during combustion, *i.e.* 1841, 1351 and 1133 °C. Furthermore, Fig. 8 shows a comparison of temperature distribution at crank angles from 20 to 30 CAD ATDC between runs 1, 2, 3 and 4. It is clear that at all crank angles, engines fueled with syngas of higher CO content, runs 2 and 4, show higher combustion temperature as compared to the other two cases, *i.e.* runs 1 and 3. It is also worth noting that when the CO₂ content is high-enough in the produced syngas, it may cause failure in internal combustion engine, *e.g.* misfire. For instance, among the observed cases, when the CO₂ content reaches 74.26% for run 5, the engine efficiency becomes negative, meaning that there is misfire happening inside the engine without any mechanical output.

Figure 7. Engine efficiency, overall efficiency and the highest temperature during syngas combustion for different experiment runs.

To have a general idea of the energetic performance of the overall waste-to-energy process, the overall efficiency, as shown in Fig. 7, is calculated through multiplying CGE and engine efficiency. The highest overall efficiency among the observed cases is found to be run 4, resulted from its high CGE, owing to its high loaded ash content and temperature, and engine efficiency, due to its

high CO content and combustion temperature. Moreover, following the optimization principle using Eq. (6), the operating condition for the highest overall efficiency is determined to be A: 25 wt%, T: 900 °C and F: 60 mL min⁻¹, with a value of 0.22, different from the optimized conditions for highest CGE, which is A: 25 wt%, T: 900 °C and F: 100 mL min⁻¹. This variance is attributed to the negative CO₂ dilution effect in the produced syngas on the engine combustion when the gasifying agent flow rate is high.

To conclude, for all the observed syngas-fueled engines with MBT ignition timing at WOT condition, the engine efficiency is found to be proportional to HHV and CO content of the produced syngas, while inversely proportional to CO₂ content, due to the low combustion temperature in ICE, contributed to by the dilution effect of CO₂ in syngas. Syngas with too high CO₂ content may cause misfire and engine failure. Lastly, the highest overall efficiency in the observed range is determined to be 0.22, under the optimized operating condition of A: 25 wt%, T: 900 °C and F: 60 mL min⁻¹.

Figure 8. Comparison of temperature distribution in ICE combustion chamber at various crank angles between different experiment runs.

With regards to scale up of the bench-scale CO₂ gasification process to pilot-scale long-term operation, the present work can serve as a preliminary study for design of parameters of the pilot-scale system. For instance, at the optimized operating conditions (A: 25 wt%, T: 900 °C, F: 60 mL min⁻¹) for the highest HHV of the produced syngas in the present study, the input CO₂/C ratio is 1.08, which can be used as a baseline for designing of the oxidant-to-feed ratio for an industrial process. Furthermore, the observed trends of performance indictors at various operating parameters can be utilized as guidance for pilot-scale experimental design as well. Addition of ash in a pilot-scale gasifier has a potential to reduce tar concentration in the produced syngas [44],

which is neglected in this bench-scale study due to insufficient time on stream of the bench-scale gasifier. Nevertheless, there are also some other issues that may require careful consideration during the scale up. Specifically, with the addition of ash to the feedstock, there might be issues, such as extra energy loss during the gasification, attributed to softening or partial melting of ash that occurs at temperatures above 750 °C [45], and dissolution of the refractory reactor wall, caused by the reaction of the released gaseous K species and silica, with the formation of particles in molten phases which may subsequently adhere to and destroy the reactor wall [46, 47].

4. Conclusions

In the present study, CO₂ co-gasification of HW and SS with addition of ash from waste as catalyst was conducted in a fixed-bed lab-scale gasifier based on Box-Behnken experiment design. The effects of three significant operating parameters, *i.e.* ash content, temperature, and gasifying agent flow rate, were investigated, with the development of mathematical models using RSM with good accuracy for optimization purpose. Finally, a KIVA-CHEMKIN based CFD model was implemented to study the combustion performance of the produced syngas in ICE, making the optimization of the present study more complete with consideration of the downstream energy utilisation. The main findings are:

- (1) The developed regression models for CGE and HHV of produced syngas show good accuracy, with R^2 equal to 0.994 and 0.989 respectively, indicating that the developed models have a good deal of reliability.
- (2) Among the three observed parameters, temperature acts as the main driving force for enhancement of CGE and HHV of produced syngas. And increase of the gasifying agent flow rate is found to positively impact CGE, whereas negatively affect HHV of the produced syngas due to the CO₂ dilution effect, and the CO₂ reduction ratio, because of the short residence time.
- (3) The increase in ash content is found to have a negative effect at the beginning, followed by a positive effect near the end on both CGE and HHV of the produced syngas at low temperature, while a nearly continuous positive effect at high temperature.
- (4) Regarding the char yield, the increase of the ash content is found to raise the char yield in terms of energy proportion at the beginning due to its catalytic effect on pyrolysis, yet followed by a decreasing trend resulted from its catalytic effect on the gasification step.

(5) Engine efficiency is found to be proportional to HHV of the produced syngas, while inversely proportional to CO₂ content, which may cause engine failure, due to the low combustion temperature in an ICE. Besides, the highest overall efficiency in the screened range of the present study is determined to be 0.22, under operating condition of A: 25 wt%, T: 900 °C and F: 60 mL min⁻¹.

In conclusion, the CO₂ co-gasification of MSWs studied in this work has shown its great potentials in enhancing the gasification reactivity, mitigating the problem of agglomeration and alleviating the greenhouse effect, through the utilization of ash from wastes as catalyst. It is considered as a more attractive option compared to the existing technologies of MSW treatment, resulted from its advantages of lowering down the gasification operating temperature and improving the throughput of the gasification facility, via cheaper catalysts from wastes.

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Nomenclature

A	ash content	wt%
a	dimensionless quantity	
A_0	turbulence model index	
AAEMs	alkali and alkaline earth metals	
ANOVA	analysis of variance	
BBD	Box-Behnken design	
CCU	carbon capture and utilization	
CGE	cold gas efficiency	
D	diffusion coefficient	m ² s ⁻¹
F	gasifying agent flow rate	mL min ⁻¹
g	specific body force	m s ⁻²
HHV	higher heating value	
$HHV_{g,syn}$	average HHV of the produced syngas	MJ Nm ⁻³

HHV_k	HHV of gas component k	MJ Nm ⁻³
HHV_s	HHV of the input solid biomass waste	MJ kg ⁻¹
$HHV_{s,ga}$	HHV of the feedstocks for gasification	MJ kg ⁻¹
HW	horticultural waste	
HWA	horticultural waste ash	
I	specific internal energy	J kg ⁻¹
ICE	internal combustion engine	
J	heat flux vector	W m ⁻²
k	turbulent kinetic energy	m ² s ⁻²
LANL	Los Alamos National Laboratory	
MBT	maximum brake torque	
$m_{s,ga}$	weight of the feedstocks for gasification	kg
MSWs	municipal solid wastes	
$n_{g,syn}$	total moles of produced syngas	mol
p	pressure of fluid	Pa
$\dot{Q}^c$	chemical source term	W m ⁻³
RSM	response surface methodology	
SS	sewage sludge	
SSA	sewage sludge ash	
STP	standard temperature and pressure	
T	temperature	°C
t	gas sampling time	min
TS%	total solids' mass percentage	
u	fluid velocity vector	m s ⁻¹
$V_{CO_2,eff}$	volume of the CO ₂ in the effluent	mL
$vol\%gas_k$	volumetric percentage of gas component k	
WOT	wide open throttle	
Y_{CGE}	predicted CGE	
y_{CO_2}	molar ratio of CO ₂	
$Y_{CO_2\text{ reduction}}$	predicted CO ₂ reduction	%
$Y_{HHV_{g,syn}}$	predicted HHV of the produced syngas	MJ Nm ⁻³
Y_i	predicted response	

Greek symbols

α	model coefficient	
ρ	density of total mass	kg m ⁻³
ρ_m	density of species m	kg m ⁻³
$\dot{\rho}_m^C$	chemical source term	kg m ⁻³ s ⁻¹
σ	viscous stress tensor	Pa
ε	dissipation rate	W kg ⁻¹

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Table 1. Box–Behnken design of gasification operating parameters.

Run No.	Ash content (A, wt%)	Temperature (T, °C)	Gasifying agent flow rate (F, mL min ⁻¹)	Biomass sample ^d (mg)	Ash sample (mg)	Feedstock (mg)
1	5(-1) ^a	700(-1)	80(0)	511	27	538
2	5(-1)	900(1)	80(0)	516	27	543
3	25(1)	700(-1)	80(0)	515	172	687
4	25(1)	900(1)	80(0)	514	171	685
5	5(-1)	800(0)	60(-1)	504	27	531
6	5(-1)	800(0)	100(1)	504	27	531
7	25(1)	800(0)	60(-1)	512	171	683
8	25(1)	800(0)	100(1)	512	171	683
9	15(0)	700(-1)	60(-1)	507	89	596
10	15(0)	700(-1)	100(1)	500	88	588
11	15(0)	900(1)	60(-1)	501	88	589
12	15(0)	900(1)	100(1)	503	89	592
13	15(0)	800(0)	80(0)	505	89	594
14 ^b	10(-0.5)	800(0)	80(0)	502	56	558
15 ^b	20(0.5)	800(0)	80(0)	504	126	630
16 ^c	0(-1.5)	800(0)	80(0)	511	0	511

^a The coded values of Box-Behnken design are presented in brackets.

^b Run 14 and 15 were added to the original Box-Behnken design for precise monitoring of ash content effect.

^c Experiment results of run 16 were used as verification for the developed mathematic models.

^d Biomass sample was a mixture of 80 wt% dry HW sample and 20wt% dry SS sample.

Table 2. Characterization of gasification feedstocks (HW, SS and ashes).

Samples	HW	SS	HWA	SSA
TS ^a (wt %)	84.82(±0.01)	16.12(±0.54)	-	-
VS ^a (wt %)	76.80(±0.01)	11.66(±0.40)	-	-
C ^b (wt%)	46.39(±0.16)	36.55(±0.43)	7.78(±0.00)	<0.5
H ^b (wt%)	5.57(±0.10)	5.37(±0.10)	<0.5	<0.5
N ^b (wt%)	0.97(±0.01)	6.21(±0.34)	ND	ND
S ^b (wt%)	ND	2.10(±0.00)	0.63(±0.01)	2.51(±0.04)
K ^b (wt%)	0.47(±0.00)	0.20(±0.00)	3.87(±0.04)	0.76(±0.00)
Ca ^b (wt%)	3.86(±0.02)	2.37(±0.03)	32.01(±0.97)	8.10(±0.03)
Na ^b (wt%)	0.03(±0.00)	0.10(±0.00)	0.14(±0.01)	0.38(±0.01)
Mg ^b (wt%)	0.28(±0.00)	0.44(±0.01)	2.49(±0.05)	1.58(±0.03)
Fe ^b (wt%)	0.03(±0.00)	2.38(±0.00)	0.19(±0.01)	8.25(±0.12)
Ash ^b (wt%)	8.94(±0.01)	26.58(±0.01)	-	-
HHV (MJ*kg ⁻¹)	15.60(±0.11)	3.00(±0.04)	-	-

^a Values calculated based on wet samples.

^b Values calculated based on oven-dried samples.

Table 3. Coefficients for syngas HHV, CGE and CO₂ reduction regression models.

Terms	Coefficients		
	Syngas HHV	CGE	CO ₂ reduction
Constant	2.55E+01	4.73E+00	2.01E+02
A	-1.34E-01	-1.62E-02	-2.35E+00
T	-7.05E-02	-1.17E-02	-6.90E-01
F	-4.54E-02	-1.68E-02	1.31E+00
A*T	7.23E-05	1.31E-05	1.68E-03
A*F	-3.92E-04	-1.44E-05	4.26E-03
T*F	-5.23E-05	1.45E-05	-1.45E-03
A ²	5.13E-03	3.73E-04	2.88E-02
T ²	5.98E-05	7.84E-06	5.55E-04
F ²	4.39E-04	4.01E-05	-1.14E-03

Table 4. The observed and statistical model predicted values of syngas HHV, CGE and CO₂ reduction.

Run No.	Syngas HHV (MJ Nm ⁻³)			CGE			CO ₂ reduction (%)		
	Observed	Predicted	Error	Observed	Predicted	Error×10 ³	Observed	Predicted	Error
1	1.05	1.22	0.16	0.08	0.08	5.30	-2.09	3.32	5.41
2	5.62	5.48	-0.13	0.50	0.50	-3.20	24.60	21.60	-2.97
3	1.90	1.99	0.09	0.14	0.14	-0.16	1.22	3.99	2.76
4	6.75	6.55	-0.20	0.62	0.61	-8.66	34.60	29.00	-5.62
5	3.37	3.31	-0.06	0.22	0.21	-7.82	8.32	6.57	-1.75
6	2.63	2.55	-0.08	0.26	0.25	-3.53	7.27	6.32	-0.95
7	4.34	4.38	0.04	0.30	0.30	0.17	8.16	8.89	0.74
8	3.29	3.31	0.02	0.33	0.33	4.46	10.50	12.10	1.54
9	1.75	1.62	-0.14	0.10	0.10	-0.42	0.39	-3.30	-3.69
10	1.03	0.91	-0.12	0.09	0.08	-4.72	8.44	3.95	-4.49
11	6.08	6.24	0.16	0.48	0.49	8.08	19.40	24.10	4.70
12	4.94	5.12	0.18	0.58	0.58	3.78	15.90	19.80	3.89
13	2.88	2.70	-0.19	0.24	0.22	-15.70	7.01	6.04	-0.97
14	2.22	2.60	0.38	0.18	0.21	32.00	4.41	5.75	1.34
15	2.80	3.06	0.26	0.23	0.25	21.80	5.77	7.77	1.99
16	3.16	3.16	0.00	0.26	0.24	-18.70	8.56	9.49	0.93

Table 5. ANOVA of the regression model for the prediction of CGE.

Source	Sum of squares	Degree of freedom	Mean square ^b	F value ^c	p-Value ^d
A	1.55E-02	1	1.55E-02	4.27E+01	3.23E-04
T	3.92E-01	1	3.92E-01	1.08E+03	6.29E-09
F	2.98E-03	1	2.98E-03	8.20E+00	2.42E-02
A*T	6.83E-04	1	6.83E-04	1.88E+00	2.13E-01
A*F	3.33E-05	1	3.33E-05	9.17E-02	7.71E-01
T*F	3.35E-03	1	3.35E-03	9.22E+00	1.89E-02
A ²	5.38E-03	1	5.38E-03	1.48E+01	6.30E-03
T ²	2.59E-02	1	2.59E-02	7.14E+01	6.42E-05
F ²	1.08E-03	1	1.08E-03	2.98E+00	1.28E-01
Model	4.47E-01	9	4.97E-02	1.37E+02	4.99E-07
Residual	2.54E-03	7	3.63E-04		
Total ^a	4.50E-01	16			

^a Sum of squares (Total) = Sum of squares (Model)+ Sum of squares (Residual)

^b Mean square= Sum of squares/Degree of freedom

^c F value= Mean square(Model)/ Mean square(Residual)

^d p-Value means the probability when the value is bigger than F value.

Figure

Figure 1. Schematic diagram of gasification experiment setup and concept of its integration with KIVA-CHEMKIN based engine CFD model.

Figure 2. XRD analysis of HWA and SSA: (a) HWA; (b) SSA.

Figure 3. Syngas composition, HHV of produced syngas and CGE for different experiment runs.

Figure 4. Response surface for the effects of ash content, temperature and gasifying agent flow rate on CGE: (a) at constant gasifying agent flow rate, 100 mL min⁻¹; (b) at constant temperature, 900 °C; (c) at constant ash content, 25 wt%; (d) predicted vs. observed plot.

Figure 5. Response surface for the effects of ash content, temperature and gasifying agent flow rate on HHV of produced syngas: (a) at constant gasifying agent flow rate, 60 mL min⁻¹; (b) at constant temperature, 900 °C; (c) at constant ash content, 25 wt%; (d) predicted vs. observed plot.

Figure 6. Char composition, char-to-feed ratio and HHV of the produced char for different experiment runs.

Figure 7. Engine efficiency, overall efficiency and the highest temperature during syngas combustion for different experiment runs.

Figure 8. Comparison of temperature distribution in ICE combustion chamber at various crank angles between different experiment runs.