Preliminary Process Design of Continuous Syngas Production in Molten Salt Gasifier

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Abstract: Pyrolysis and CO_2 gasification were experimentally investigated by direct dispersion of cellulose powder in a high-temperature molten salt (MS) system. Ni/Al_2O_3 catalyst powder was suspended in MS (CLMS) to improve the production rate and yield of syngas in both cellulose pyrolysis and char gasification. A combined pyrolysis-CO_2 gasification process (CPG) is known to provide CO-rich syngas which is primarily attributable to H_2 consumption during the reverse water gas shift reaction (RWGS). In this study, a separated pyrolysis-CO_2 gasification process (SPG) was proposed to produce H_2-rich syngas. Four conceptual process designs, namely, SPG in MS, SPG in CLMS, CPG in MS, and CPG in CLMS were examined. As an idealized operating condition, the present design basis assumed that all of the pyrolysis-generated CO_2 by-product could essentially be consumed in the char gasification step of the CPG. Based on a design basis of 100 kmol/h cellulose feed, the CPG produced 593 kmol/h of syngas in MS and 485 kmol/h in CLMS with an overall H_2:CO mole ratio of 0.21 and 0.14, respectively. In contrast, the corresponding values of the SPG were 770 kmol/h in MS and 1,137 kmol/h in CLMS with ratios of 0.58 and 0.76, respectively. In addition, the SPG could reduce the residual char to 33 kmol/h in MS and to 30 kmol/h in CLMS from 239 kmol/h and 268 kmol/h of its CPG counterparts. The required total reactor volumes of the SPG were approximately half of the corresponding CPG. Similarly, the total heat consumption required for the SPG was also slightly less. When the present results were compared to our previous work which assumed from the actual experimental condition that the CO_2 required for char gasification was fed stoichiometrically equal to the moles of the residual char, the present corresponding values of mass flow rate of salt, heat consumption rate and syngas/heat input were found to decrease 1% for the SPG and 7% for the CPG mainly due to savings in heating up the smaller CO_2 feed. In conclusion, the SPG in CLMS embodied the most effective system design in terms of the quantity and quality of the syngas, the reduced residual char as well as the effective utilization of concentrated solar energy.

Keywords: Syngas; Pyrolysis; CO_2 gasification; Ni/Al_2O_3; Conceptual process design.

1. Introduction

Recognized as the solar heat storage and carrier of choice, molten salt could also serve well as reaction medium for endothermic reactions [1]. Solar pyrolysis by direct dispersion of biomass particles in high-temperature molten salt (MS) could provide high-quality syngas with negligible tar and low char residue [2]. The reported results are similar to those of fast pyrolysis in which biomass particles were rapidly heated to high temperature to yield syngas, liquid bio-oils and char, as shown ideally in Eq. 1 [3]. In high-temperature molten salt environment, these liquid products were subsequently decomposed to additional gas products, though char would still remain [2, 4].

$$C_6H_{10}O_{5\,(s)} \rightarrow 5(CO_{(g)} + H_{2(g)}) + C_{(s)}, \Delta H^\circ_{@298K} = +425 \text{ kJ} \cdot \text{mol}^{-1} \quad (1)$$
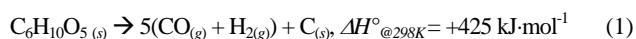
However, the stubborn char could be gasified in the presence of a suitable gasifying agent. Hathaway et al. [5] found that steam gasification of cellulose in molten salt could provide H_2-rich syngas but the salt might be partially decomposed by steam. Since CO_2 could maximize the stability of carbonate salts [6], allow a safe-feed operation compared to steam (risk of molten salt bath "explosion" due to "carry-over" of bulk condensate water resulting in explosive generation of steam) and constitute an increasing global warming gas, CO_2 was selected as gasifying agent to accomplish char gasification following Boudouard reaction (Eq.(2)) [7], thereby producing additional CO product gas.

$$C_{(s)} + CO_{2(g)} \rightarrow 2CO_{(g)}, \Delta H^\circ_{@298K} = +172 \text{ kJ} \cdot \text{mol}^{-1} \quad (2)$$

Catalytic gasification of char in molten salt in Eq. 2 can be explained by a two-step mechanism [8]. A plausible mechanism in the case of an alkali carbonate salt was proposed [7]. First, the carbonate salt reacted with carbon according to Eq. 2.1

$$M_2CO_3 + 2C \rightarrow 2M + 3CO \quad (2.1)$$

According to our TGA analysis of char in MS and CLMS, the above reaction took off at temperature above 700°C. Next the alkali metal reacted with CO_2 to yield CO.

$$2M + 2CO_2 \rightarrow M_2CO_3 + CO \quad (2.2)$$

By regenerating the alkali metal to salt, CO_2 can effectively stabilize the salt. As shown in Fig. 1(a), continuous solar gasification of cellulose by feeding CO_2 directly to a suspension of cellulose powder in molten salt involves two concurrent stages: (I) cellulose pyrolysis and (II) char gasification.

In this combined pyrolysis-CO_2 gasification process (CPG) in Fig. 1(b), some of the H_2 fraction in the produced syngas inevitably reacted with the CO_2 gasifying agent to produce additional CO and H_2O via the reverse water gas shift (RWGS) reaction (Eq. (3)), thereby drastically decreasing the typical H_2/CO ratio [9].

$$H_{2(g)} + CO_{2(g)} \rightarrow CO_{(g)} + H_2O_{(g)}, \Delta H^\circ_{@298K} = +40.28 \text{ kJ} \cdot \text{mol}^{-1} \quad (3)$$
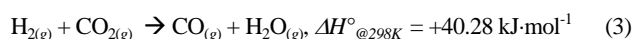
Therefore, a separated pyrolysis-CO_2 gasification process (SPG) as depicted in Fig. 1(b) was proposed to independently produce H_2-rich syngas and CO-rich product gas by minimizing the RWGS effect. In the SPG process, cellulose was pyrolyzed by solar-heated molten salt inside the pyrolysis unit and the obtained char, floating up [2] due to its low density, was transferred along with the MS stream to the CO_2 gasification unit. Optionally, both cellulose pyrolysis and CO_2 gasification of char could be catalytically enhanced by loading Ni/Al_2O_3 catalyst

in the MS. It is common knowledge that CH_4 is as a byproduct of cellulose pyrolysis reactions [3]. The catalyst loaded-molten salt (CLMS) could significantly increase H_2 production yield while decreasing yield of CH_4 via CO_2 dry reforming reaction [10] as shown in Eq. (4).

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO, \Delta H°_{@298K} = +247 \text{ kJ·mol}^{-1} \quad (4)$$
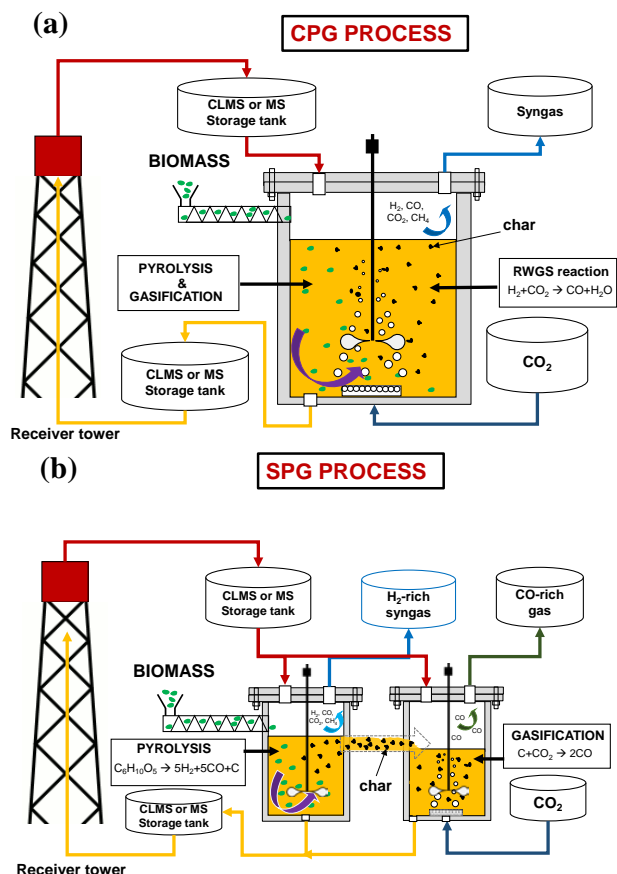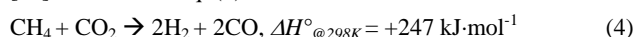
(a)

Fig. 1 Schematics of (a) CPG process and (b) SPG process.

The objective of the present investigation was to carry out and compare 4 conceptual process designs, namely, SPG in MS, SPG in CLMS, CPG in MS, and CPG in CLMS. As an idealized operating condition, the present design basis assumed that all of the pyrolysis-generated CO_2 by-product could essentially be consumed in the char gasification step of the CPG. This assumption was intended to favor the performance of the CPG against the SPG. In addition, the present results were compared to our previous work [11], which assumed from the actual experimental condition that the CO_2 required for char gasification was fed stoichiometrically equal to the moles of the residual char. Obviously this assumption was unfavorable to the CPG.

2. Methodology

To obtain basic data for conceptual process design, cellulose pyrolysis and CO_2 gasification of char in both MS and CLMS were separately carried out in a lab-scale tubular reactor made of dense alumina [8, 9] as shown in Fig. 2.

A eutectic carbonate salt blend of Na, K, and Li with a melting point of 397°C [4] was used as reaction medium. 15%Ni/Al_2O_3 catalyst powder was prepared via impregnation of nickel nitrate onto γ-Al_2O_3 (~75 μm particle size), followed by calcination in air and reduction in H_2 flow at 850°C for 4 and 2 h, respectively [10]. To obtain CLMS, the said catalyst was loaded in MS with a fixed 7wt% [8] of the catalyst to MS by grinding [8, 9]. Microcrystalline cellulose powder (~38 μm) and

carbonized sawdust char were used, respectively, as model biomass and char. In detail, the gasification was carried out in a tubular reactor made of dense alumina (id. = 33 mm, 1200 mm effective length) heated by an electric furnace (model ARF-3050, 100V, 500W, Asahi) with a PID controller (KP 1000, Chino). The mass ratio of the MS or CLMS medium to feedstock was fixed at 140 to standardize the quantitative effect of the medium. A mixture of the feedstock and the MS or CLMS was loaded into a ceramic boat center-positioned inside the reactor tube. The reactor was heated to a target temperature of 600-900°C at a heating rate of 20°C/min under CO_2 flow (Purity>99.999%) of 100 mL/min. After passing through a gas filter (PTFE membrane filter, pore size <20 nm, ADVANCETEC), a small sample of gas products was taken every 5 min with a 5-mL calibrated gas-tight syringe and then analyzed with Gas Chromatography equipped with TCD detector (Shimadzu GC-8A) to determine the time-dependent gas composition. To determine the total amount and average composition of gas products, total gas product was entirely collected in a 20-litre polyvinylidene fluoride (PVDF) gas bag while its flow rate at room temperature was continuously recorded by a flow meter (calibrated by film flow meter, VP-3, 20-1000nL/min, STEC) [8]. Gas product yields and production rates resulting from sudden feed of cellulose to the high-temperature MS were used as base case for calculation [4]. This is similar to our conceptual process design in which cellulose is directly fed to high-temperature MS reservoir [2, 4]. The observed catalytic enhancement effects of Ni/Al_2O_3 catalyst [8, 9] and the RWGS effect [9] on product gas yields from our experiments were used in the design calculations of both SPG and CPG processes. It was assumed that the catalytic enhancement effect in the continuous conceptual design was the same as our batch experiments. Unmeasured data, such as amount of condensed H_2O product [2] was estimated from overall elemental balances of H, C and O.
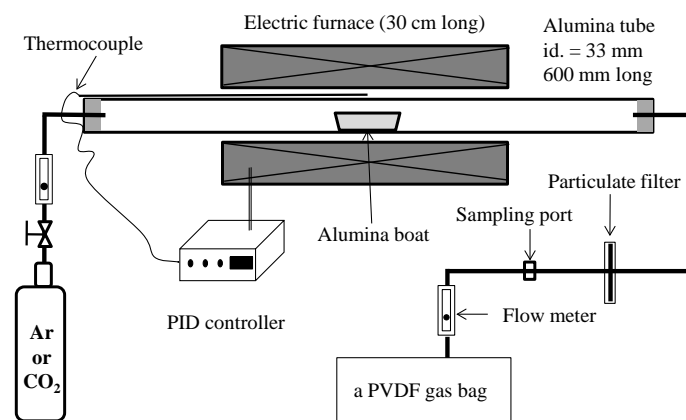

Figure 2. Schematics of experimental setup for cellulose pyrolysis and CO_2 gasification of char in MS and CLMS.

According to previous studies [2, 4], cellulose feed of 100 kmol/h (16,200 kg/h), average reaction temperature of 800°C, a predetermined appropriate temperature, and atmospheric pressure were used as our mini-plant design basis. The same residence times (τ) as required for reaction completion in batch experiments (τ_p = 100s for cellulose pyrolysis and τ_g = 3300s for CO_2 gasification of char) were used [4, 12]. Taking account of the estimated temperature drop [4], the inlet and outlet temperatures of MS/CLMS (T_{MS-in}, T_{MS-out}, $T_{CLMS-in}$, $T_{CLMS-out}$) were determined to be 950 and 800°C, respectively. Uniform temperature every point inside the reactor, perfect mixing, and no heat-mass transfer limitation were assumed. Required volume and flow rate of MS/CLMS (M) and total heat consumption rate (Q_T) were calculated using heat of reactions (mainly pyrolysis,

char gasification, and RWGS) [2, 8, 9], the predetermined salt temperature difference of 150°C [2] and the residence times [4, 12]. Molar flowrate of CO_2 gasifying agent was set equal to that consumed by the pyrolyzed char according to the char conversion from experimental results [9] and the temperature was set at 200°C [13]. Since the pyrolysis reaction was fast [2-4], the resulting char was transferred rapidly to the char gasification unit, whereas the carbonate-assisted gasification reaction as proposed in Eq. 2.1 was neglected in the pyrolysis unit. As shown in Eq. 2.1-2.2, a shorter residence time of CO_2 in molten salt compared to that of char should not affect the Boudouard reaction in this continuous process because char would react with salt to yield alkali metal while CO_2 would react with the metal to regenerate the carbonate salt.

3. Results and Discussion

3.1 Catalytic enhancement effect on SPG and CPG

Experimental yields of gas products and char with and without catalytic enhancement by Ni/Al_2O_3 catalyst as well as RWGS effect on syngas yields from each process are listed in Table 1.

CO yields could originate from cellulose pyrolysis, CO_2 gasification of char, and RWGS. CO_2 and char yields originated from pyrolysis while the idealized operating condition required that there was no CO_2 excess from char gasification. Similar to the SPG process in Fig. 1(b), experiments 1 and 2 in Table 1 on cellulose pyrolysis in argon and CO_2 gasification of char in both MS and CLMS were carried out separately. For a base case of

cellulose pyrolysis under argon flow [4] and CO_2 gasification of char in MS (catalyst-less molten salt) [9], the experimental results in **Table 1** showed that the production yields of H_2, CO, CH_4, CO_2, and balanced H_2O were 2.82, 3.40, 0.91, 0.62, and 0.36 mole per mole of cellulose, respectively, while char yield was about 1.07 mole per mole of cellulose (7.9 wt%) [4]. Since a small amount of tar (less than 1 wt%) [4] was experimentally observed on HEPA filter, it was neglected in the design calculation of conceptual processes. Meanwhile, CO_2 gasification of char was experimentally found to provide CO yield of 1.47 mole per mole of starting cellulose and residual char of 0.33 mole per mole of cellulose. Under equivalent conditions in CLMS (catalyst-loaded molten salt, 7wt% of $15\%Ni/Al_2O_3$ in MS), our experimental results revealed that the pyrolysis yields of H_2, CO, and char were raised to 4.91, 4.36, and 1.35 mole per mole of cellulose (increased by 74, 28, and 26%, respectively), while undesired CH_4 and CO_2 yields dropped to 0.01 and 0.29 mole/mole of cellulose (decreased by 99% and 53%, respectively). H_2O yield of 0.07 mole/mole was calculated from overall elemental balances. Char yield obtained from cellulose pyrolysis in catalyst-loaded molten salt (CLMS) was 1.35 mole/mole of cellulose (10 %wt). The slightly increased char yield by 26% (from 1.07 to 1.35 mole per mole of cellulose) was ascribed to the effect of nickel catalyst. Similarly, in CO_2 gasification of char in CLMS, catalytic enhancement by Ni/Al_2O_3 was observed to increase the char conversion from 0.69 for MS to 0.78 for CLMS in Fig. 3(a) and (b), thus reducing residual char from 0.33 to 0.30 mole per mole of cellulose.

Table 1. Summary of production yields, catalytic enhancement, and RWGS effects.

Experiment	H_2	CO^a	CO^b	CH_4	$CO_2{}^c$	H_2O^d	C^e	C^f
1. SPG in MS [mol/mol cellulose] (base case*)	2.82	3.40	1.47	0.91	0.62	0.36	1.07	0.33
2. SPG in CLMS [mol/mol cellulose]	4.91	4.36	2.10	0.01	0.29	0.07	1.35	0.30
3. CPG in MS [mol/mol cellulose]	0.58	4.27		0.59	1.80	3.23	4.95	
4. CPG in CLMS [mol/mol cellulose]	1.02	4.91		0.18	1.80	3.63	5.66	

Note: * = gas yields from cellulose pyrolysis [4] and CO_2 gasification of char [9]
a = CO production yield from cellulose pyrolysis
b = CO production yield from CO_2 gasification of char
c = CO_2 production yield from pyrolysis reaction
d = H_2O production yields calculated from elemental balance
e = char yield from cellulose pyrolysis
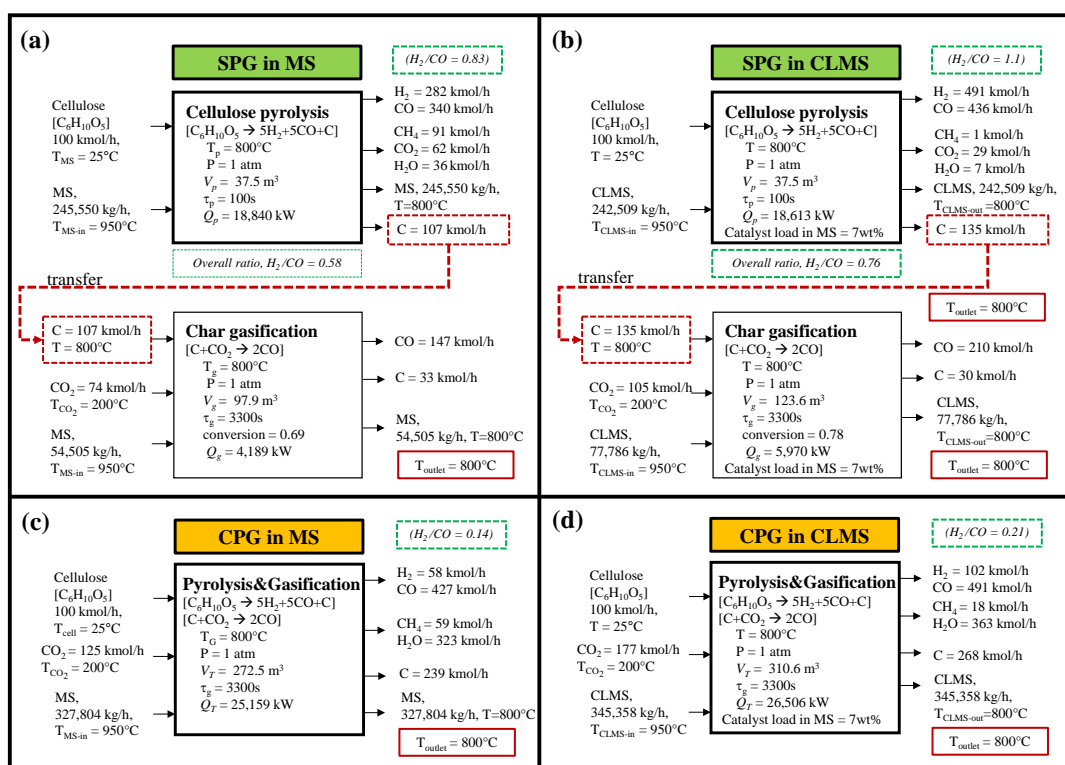f = char remaining from CO_2 gasification of cellulose-derived char

Figure 3. Flow charts of (a) SPG in MS, (b) SPG in CLMS, (c) CPG in MS, and (d) CPG in CLMS.

Table 2. Summary of key results from four conceptual process designs.

Process	V_p [m³]	V_g [m³]	V_T [m³]	Input						Output [kmol/h]						H_2/CO	Syngas/Heat [kmol/kW]
				Cellulose [kmol/h]	CO_2 [kmol/h]	M [kg/h]	Q_p[kW]	Q_g[kW]	Q_T[kW]	H_2	CO	CH_4	CO_2	H_2O	C		
1. SPG in MS	37.5	97.9	135.4	100	74	300,055	18,840	4,189	23,029	282	488	91	62	36	33	0.58	0.033
2. SPG in CLMS	37.5	123.6	161.1	100	135	320,295	18,613	5,970	24,583	491	646	1	29	7	30	0.76	0.046
3. CPG in MS	–	–	272.5	100	125	327,804	–	–	25,159	58	427	59	0	323	239	0.14	0.019
4. CPG in CLMS	–	–	310.6	100	177	345,357	–	–	26,506	102	491	18	0	363	268	0.21	0.022

Note: V_T = Total volume of molten salt with/without catalyst [m³], $V_T = V_p + V_g$ for SPG process (see **Fig. 3**)

$\quad\quad$ M = Mass flowrate of molten salt with/without catalyst [kg/h]

$\quad\quad$ Q_T = Total heat input [kW], $Q_T = Q_p + Q_g$ for SPG process (see **Fig. 3**)

For experiments 3 and 4 in Table 1, direct CO_2 gasification of cellulose (similar to the CPG in Fig. 1(a)) was carried out in the lab-scale batch reactor for both MS and CLMS for comparison. Here the reactions including cellulose pyrolysis and CO_2 gasification of pyrolyzed char proceeded concurrently. Compared to the case of MS, our experimental results revealed that the CPG in CLMS experiment could increase total yields of H_2, CO, char, and H_2O from 0.58, 4.27, 2.39, and 3.23 to 1.02, 4.91, 2.68, and 3.63 mole/mole of cellulose, respectively. However CH_4 yield was decreased from 0.59 to 0.18 mole per mole of cellulose ascribed to CH_4 reforming by nickel catalyst, while CO_2 yield was the same. Compared to SPG experiments, the corresponding H_2 yield considerably decreased from 2.82 and 4.91 for SPG experiments to 0.58 and 1.02 for CPG experiments, respectively, due to the RWGS (Eq. 3). As a result, the CO yields were increased from 3.40 and 4.36 to 4.27 and 4.91 mole per mole of cellulose. Interestingly, compared to the base case, significant decreases in CH_4 yield were observed for both CPG in MS and CLMS, which can be ascribed to CO_2 dry reforming reaction between CH_4 and CO_2 in molten salt (Eq. 4) as well as catalytic enhancement of Ni/Al_2O_3 on CH_4 reforming [10].

3.2 Conceptual process design of continuous solar gasification of cellulose

Fig. 3 shows the detailed flow charts with stoichiometric calculation results for the four conceptual process designs of continuous solar gasification of cellulose which correspond to the depicted processes in Fig. 1, namely, (a) SPG in MS, (b) SPG in CLMS, (c) CPG in MS, and (d) CPG in CLMS. In addition, all key results are summarized in Table 2.

Obviously, the SPG in both MS and CLMS would require less total volume of molten salt (V_T), total heat input (Q_T), and mass flowrate of molten salt (M) compared to both of the CPG. In addition, syngas yield nearly doubled, while byproducts considerably decreased. The H_2:CO ratio in the SPG increased more than 3 times above the CPG, while the syngas/heat input ratio also nearly doubled. Clearly, the SPG processes were much more efficient for the continuous solar gasification in molten salt. Comparison between the SPG in CLMS and its CPG counterpart revealed that the former produced 1,137 kmol/h of syngas with overall H_2:CO ratio of 0.76 (the ratio being 1.1 for only the pyrolysis process), whereas the corresponding values for the CPG were 593 kmol/h and 0.21, respectively. It should be noted that the increased syngas obtained from the SPG in CLMS would require smaller adjustment of H_2:CO ratio for chemical synthesis [14]. In addition, the high-purity CO product gas from SPG second unit may be conveniently used as raw material for synthesis of chemicals from CO. In fact, the SPG in CLMS also reduced the residual char to 30 from 268 kmol/h of the CPG. Equally significant is the fact that total salt volume of the SPG in CLMS ($V_T = V_p + V_g = 37.5 + 123.6 = 161.1$ m³) was nearly half of its CPG counterpart ($V_T = 310.6$ m³) while total heat required (Q_T) was 8% less (24,583 kW vs. 26,506 kW).

In Fig. 3, comparison between the 2 SPG processes in MS (a) and CLMS (b) reveals that the Ni/Al_2O_3 catalyst could greatly increase H_2 yield from 282 kmol/h to 491 kmol/h and total syngas yield from 769 kmol/h (282+340+147 = 769 kmol/h) to 1137 kmol/h (491+436+210 = 1,137 kmol/h) with an overall H_2:CO ratio of 0.58 and 0.76, respectively. Meanwhile, all undesired byproduct yields in Table 2 decreased significantly, especially that of CH_4. In other words, syngas yield increased to nearly 1.5 times while the H_2:CO ratio increased to 1.3 times due to Ni/Al_2O_3 catalytic enhancement on both cellulose pyrolysis and CO_2 gasification of char. This indicates that Ni/Al_2O_3 could actively catalyze the reaction toward more production of H_2 and CO, and reduce the CH_4 yield even in the high-temperature molten salt. The required total volume of molten salt storage for SPG in CLMS ($V_T = 161.1$ m³) was 19% larger than SPG in MS ($V_T = V_p + V_g = 37.5 + 97.9 = 135.4$ m³). This could be ascribed to the increased pyrolysis char yield (from 107 to 135 kmol/h) due to nickel catalyst in CLMS. Although the SPG in CLMS required slightly larger total salt volume and total heat input than the SPG in MS, it showed much more attractive results in terms of the syngas yields and quality. Therefore, the SPG in CLMS could realize a more productive and economical process than the SPG in MS.

When the present design results were compared to our previous work, which assumed from the actual experimental condition that the CO_2 required for char gasification was fed stoichiometrically equal to the moles of the residual char, the present corresponding values of mass flow rate of salt (M), and heat consumption rate (Q_T) were found to decrease 1% for the SPG and 7% for the CPG mainly due to savings in heating up the smaller CO_2 feed. Though the idealized operating condition led to a small energy saving effect compared to our previous design results, in practice we should endeavor to approach this idealized condition because we can expect significant cost savings in the subsequent gas separation process.

4. Conclusions

The Ni/Al_2O_3 catalyst significantly enhanced the syngas yield and increased char conversion while reducing byproduct CH_4 yield. Based on stoichiometric verification, both SPG processes required less total salt volume, less total heat input, and less mass flowrate of molten salt when compared to both CPG processes. Syngas yield nearly doubled, while undesirable byproducts considerably decreased, especially CH_4. The H_2:CO ratio in the SPG processes increased 3 times higher than the CPG processes, while the syngas/heat input ratio doubled. The required total reactor volume of SPG in CLMS was about a half of that in CPG counterpart. Similarly, the total heat required was 8% lower while the residual char decreased as much as 9 folds. When compared to our previous work, the present values of mass flow rate of salt and heat consumption rate were found to decrease 1% for the SPG and 7% for the CPG mainly due to savings in heating up the smaller CO_2 feed. In conclusion, the SPG in CLMS embodied the most effective system design in terms of the quantity and quality of the syngas, the reduced residual char as well as the effective utilization of concentrated solar energy.

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Abbreviations

MS	molten salt
CLMS	catalyst-loaded molten salt
RWGS	reverse water gas shift reaction
CPG	combined pyrolysis-CO_2 gasification process
SPG	separated pyrolysis-CO_2 gasification process

Nomenclature

$\Delta H°$	heat of reaction [kJ·mol^{-1}]
V_T	total volume of molten salt with/without catalyst [m^3]
V_p	volume of molten salt with/without catalyst in pyrolysis reactor [m^3]
V_g	volume of molten salt with/without catalyst in gasifier [m^3]
Q_T	total heat input [kW]
Q_p	heat input for pyrolysis reactor [kW]
Q_g	heat input for gasifier [kW]
M	mass flowrate of molten salt with/without catalyst [kg/h]
T_{CO2}	temperature of CO_2 feed [°C]
T_{MS-in}	inlet temperature of molten salt [°C]
$T_{MS-outlet}$	outlet temperature of molten salt [°C]
$T_{CLMS-outlet}$	inlet temperature of catalyst-loaded molten salt [°C]
$T_{CLMS-outlet}$	outlet temperature of catalyst-loaded molten salt [°C]
T_{outlet}	outlet temperature of all products [°C]
P	pyrolysis reactor/gasifier pressure [atm]
τ_p	residence time for pyrolysis [s]
τ_g	residence time for char gasification [s]

Highlights

➤ The conceptual process design of continuous biomass gasification in molten salt (MS) was examined.

➤ The combined pyrolysis-CO_2 gasification process (CPG) and separated pyrolysis-CO_2 gasification process (SPG) in CLMS and MS was examined and compared.

➤ The Ni/Al_2O_3 catalyst loaded in molten salt (CLMS) improved both production rate and yield of syngas.

➤ The catalyst enhanced both the production rate and yield the pyrolysis and char gasification.

➤ The SPG in CLMS exhibited the most effective process for syngas production