Biomass-to-syngas production in catalyst-loaded molten salt: catalytic enhancement and conceptual process design

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Abstract:
Pyrolysis and CO_2 gasification were experimentally investigated by direct dispersion of cellulose powder in high-temperature molten salt system (MS). Ni/Al_2O_3 catalyst was loaded in molten salt (CLMS) to improve the production rate and yield of syngas in both cellulose pyrolysis and CO_2 gasification of the pyrolyzed char. A combined CO_2 pyrolysis-gasification (CPG) process is known to provide CO-rich syngas while H_2 fraction decreased due to the reverse water gas shift reaction (RWGS). In this study, a two-step separate pyrolysis-CO_2 gasification (SPG) process in catalyst-loaded molten salt (CLMS) was proposed to avoid this problem. Four conceptual process designs, namely, SPG in MS, SPG in CLMS, CPG in MS, and CPG in CLMS were carried out and their results compared. Based on a design basis of 100 kmol/h (16,200 kg/h) of cellulose feed, the CPG in MS and CLMS produced 593 kmol/h and 485 kmol/h of syngas with an overall H_2:CO ratio of 0.21 and 0.14, respectively, whereas the corresponding values of the SPG in MS and CLMS were 770 kmol/h and 0.58, and 1,137 kmol/h and 0.76, respectively. In addition, the SPG in MS reduced the residual char to 33 from 268 kmol/h for its CPG counterpart. Similarly, SPG in CLMS reduced the residual char to 30 from 239 kmol/h for its CPG counterpart. The required total reactor volumes of SPG (135.4 m^3 in MS and161.1 m^3 in CLMS) were about half of CPG (272.5 m^3 in MS and 310.6 m^3 in CLMS). The total heat required for SPG (23,308 kW in MS and 24,832 kW in CLMS) was significantly less than that of CPG (28,404 kW in MS and 26,814 kW in CLMS). The Ni/Al_2O_3 could enhance the syngas yield, reduced CH_4 yield, and increase char conversion. The SPG process in CLMS could exhibit the most effective arrangement of gasifier in terms of both quantity and quality of syngas products, char residual, as well as effective utilization of solar energy.

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

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1. Introduction

Molten salt, the solar heat storage and carrier of choice, could serve as reaction medium for endothermic reactions. 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 (Adinberg et al., 2004). The process is similar to fast pyrolysis (as shown ideally in Eq. (1)) in which biomass particles are rapidly heated to high temperature to yield syngas, liquid bio-oils, and solid product as char. In high-temperature molten salt environment, such liquid products are subsequently decomposed to additional gas products, while char is still remain in salt melt.

$$C_6H_{10}O_{5\,(s)} \rightarrow 5(CO_{(g)} + H_{2(g)}) + C_{(s)}, \qquad \Delta H°_{@298K} = +425\ kJ{\cdot}mol^{-1} \qquad (1)$$

However, the obtained char could be further gasified by adding suitable gasifying agent. Hathaway et al. (Hathaway et al., 2011) found that steam gasification (steam as gasifying agent) of cellulose in molten salt could provide H_2-rich syngas but the salt might be partially decomposed by the strongly oxidizing characteristics of steam. Since CO_2 gas could maximize the stability of salt and provide an easy-feed operation compared to steam (risk in molten salt bath "explosion": i.e. explosive generation of steam due to condensate bulk water "carry-on") as well as environmental friendly benefits, it was selected as gasifying agent to complete char gasification following Boudouard reaction (Eq.(2)), thereby additional CO product gas is produced.

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

However, CO_2 gasification of char in molten salt consists of two-step mechanisms. The proposed mechanism of char gasification in the alkali carbonate salt is as follows (Kapteijn et al., 1983). First, the carbonate salt reacts with carbon according to Eq. 2.1.

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

Next, the alkali metal reacts with CO_2 to yield CO.

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

Thus, CO_2 is suitable for gasification in molten salt because it can stabilize the salt and recycle the alkali metal to salt. However, solar gasification of cellulose by direct CO_2 feed to gasify cellulose powder in molten salt consists of two main concurrent stages of (I) cellulose pyrolysis and (II) char gasification by CO_2 as shown in Fig. 1(a). In such combined CO_2 pyrolysis-gasification (CPG) process, the H_2 fraction in syngas inevitably reacted with excess CO_2 gasifying agent to additional CO and water according to the reverse water gas shift (RWGS) reaction (Eq. (3)), thereby greatly decreasing the H_2/CO ratio as compared to a sole cellulose pyrolysis process (Ratchahat et al., 2014b).

$$H_{2(g)} + CO_{2(g)} \rightarrow CO_{(g)} + H_2O_{(g)}, \qquad \Delta H°_{@298K} = +40.28 \text{ kJ·mol}^{-1} \qquad (3)$$

In this study, a two-step separate pyrolysis-CO_2 gasification (SPG) process as shown in Fig. 1(b) was, therefore, proposed and investigated to minimize such RWGS effects and separately produce H_2-rich syngas and CO-rich product gas.

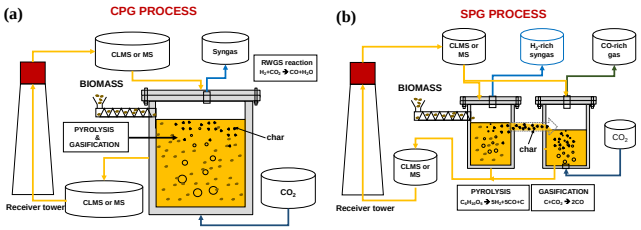

Fig. 1 Schematics of (a) CPG process and (b) SPG process.

In the SPG process, cellulose is pyrolyzed by solar heat in molten salt inside the first unit of pyrolysis and then the obtained char floating up due to its low density was transferred to the second unit of CO_2 gasification. Catalytic enhancement of molten salt system for both cellulose pyrolysis and CO_2 gasification of char was improved by adding Ni/Al_2O_3 catalyst. CH_4 is one of by-products from cellulose pyrolysis reactions. The catalyst loaded-molten salt (CLMS) could increase H_2 production yield by decreasing yield of CH_4 by-product *via* CO_2 dry reforming reaction as shown in Eq. (4).

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

In all, four conceptual process designs at mini-plant scale including SPG in MS, SPG in CLMS, CPG in MS, and CPG in CLMS were carried out to provide quantitative evidences for comparison and the key calculation results were discussed.

2. Methodology

To obtain basic data for conceptual process design, the cellulose pyrolysis and the CO_2 gasification of char in both MS and CLMS were separately carried out in a lab-scale tubular reactor made of dense alumina as shown in Fig. 2. A eutectic carbonate salt blend of Na, K, and Li with a melting point of 397°C, was used as gasification medium. 15%Ni/Al_2O_3 catalyst powder was prepared via simple 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. To obtain CLMS, the Ni/Al_2O_3 catalyst was loaded in MS with a fixed 7wt% of the catalyst to MS by simply grinding. Microcrystalline cellulose powder (~38 µm) and carbonized sawdust char were used, respectively, as model biomass and char. Detail of experimental conditions and procedure was described

elsewhere (Ratchahat et al., 2014a). Gas product yields resulting from sudden feed of cellulose tablet to the molten salt at high temperature were used as base case for calculation. This is similar to our conceptual design in which cellulose is directly fed to high-temperature molten salt reservoir. The obtained catalytic enhancement effects of Ni/Al_2O_3 catalyst and the RWGS effect on product gas yields from our experiments were used in the conceptual design calculations of both SPG and CPG processes. It is assumed that the catalytic enhancement in the continuous conceptual design was the same as our batch experiments. Unmeasured data, such as amount of condensed H_2O product was estimated from overall elemental balances of H, C and O.

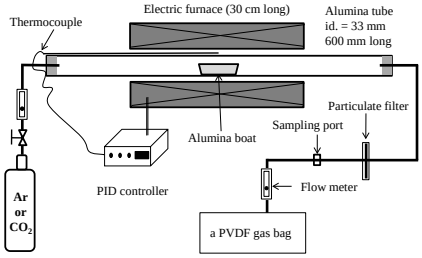

Fig. 2 Schematics of experimental setup for cellulose pyrolysis and CO_2 gasification of char in MS and CLMS.

Cellulose feed of 100 kmol/h (16,200 kg/h), average reaction temperature of 800°C at atmospheric pressure was considered as our mini-plant design basis using the same residence times (τ) as required for reaction completion in the batch experiments (100s for cellulose pyrolysis and 3300s for CO_2 gasification of char) (Hathaway et al., 2011 and Yoshida et al., 1999). Inlet and outlet temperatures of molten salt were 950 and 800°C, respectively. Required volume of molten salt and heat input were calculated using heat of reactions, the predetermined salt temperature difference of 150°C and the residence time. Molar flowrate of CO_2 gasifying agent was set stoichiometrically equal to that of the incoming pyrolyzed char according to Eq. 2. As shown in Eq. 2.1-2.2, a shorter residence time of CO_2 in molten salt compared to that of char would 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

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 are listed in Table 1. CO production yields could originate from pyrolysis, CO_2 gasification of char, and RWGS. On the other hand, CO_2 and char yields originated from pyrolysis and CO_2 gasification, respectively. In processes 1 and 2, experiments on cellulose pyrolysis in argon and CO_2 gasification of char in both MS and CLMS were carried out separately similar to Fig. 1(b). In case of cellulose pyrolysis in MS (catalyst-less molten salt) under argon flow (base case), experimental results 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/mole of cellulose, respectively, while char yield was about 1.07 mole/mole of cellulose (7.9 wt%) (Hathaway et al. 2011). Since a small amount of tar (less than 1 wt%) was observed on HEPA filter, it could be neglected in the calculation (Hathaway et al., 2011). Meanwhile, CO_2 gasification of char was experimentally found to provide CO yield of 1.47 mole/mole of cellulose. Under equivalent conditions in catalyst-loaded molten salt (CLMS, 7wt% of 15%Ni/Al_2O_3 in MS), our experimental results revealed the pyrolysis yields of H_2, CO, and char were elevated to 4.91, 4.36, and 1.35 mole/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 balance. Similarly, in CO_2 gasification of char, catalytic

enhancement by Ni/Al_2O_3 was observed to increase char conversion from 0.69 for MS to 0.78 for CLMS, thus resulting in residual char being reduced from 0.33 to 0.30 mole/mole of cellulose.

For processes 3 and 4 in Table 1, direct CO_2 gasification of cellulose (similar to CPG process of Fig. 1(a)) was carried out in both MS and CLMS for comparison. Here cellulose pyrolysis and CO_2 gasification of pyrolyzed char proceeded concurrently. Our experimental results revealed that, compared to the case of MS, CO_2 gasification of cellulose in CLMS could increase total yields of CO, CO_2, and char while considerably decreased H_2 yield from 1.02 to 0.58 mole/mole of cellulose because excess CO_2 gasifying agent would react with the produced H_2 to yield more CO at 3.27 compared to 2.88 mole/mole of cellulose (via Eq. (3)). 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. As expected, when cellulose was gasified in CLMS, H_2 and CO yields due to RWGS increased above those in MS due to hydrogenation effect of nickel catalyst.

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

Process	H_2	CO^a	CO^b	CO^c	CH_4	$CO_2{}^d$	$CO_2{}^e$	H_2O^f	C^g	C^h
1. SPG in MS [mol/mol cellulose] (base case*)	2.82	3.40	1.47	-	0.91	0.62	0.33	0.36	1.07	0.33
2. SPG in CLMS [mol/mol cellulose]	4.91	4.36	2.10	-	0.01	0.29	0.30	0.07	1.35	0.30
3. CPG in MS [mol/mol cellulose]	0.58	1.04	0.35	2.88	0.59	1.80	2.39	3.23	2.56	2.39
4. CPG in CLMS [mol/mol cellulose]	1.02	1.04	0.60	3.27	0.18	1.80	2.68	3.63	2.98	2.68

Note: * = gas yields from cellulose pyrolysis (Hathaway et al., 2011) and CO_2 gasification of char (Ratchahat et al., 2014b), [a] = CO production yield from cellulose pyrolysis in argon, [b] = CO production yield from CO_2 gasification of char from cellulose pyrolysis, [c] = CO production yield from RWGS reaction, [d] = CO_2 production yield from pyrolysis reaction, [e] = CO_2 excess from CO_2 gasification of char, [f] = H_2O production yields calculated from elemental balance, [g] = char yield from cellulose pyrolysis, [h] = char remaining from CO_2 gasification of cellulose-derived char

3.2 Conceptual design of continuous solar gasification of cellulose

Fig. 3 shows the completed flow charts with all key calculation results for the four conceptual process designs of continuous solar gasification of cellulose, namely, (a) SPG in MS, (b) SPG in CLMS, (c) CPG in MS, and (d) CPG in CLMS processes. In addition, all key results are summarized in Table 2. Obviously, the SPG processes in both MS and CLMS would require less total volume of molten salt (V_r), total heat input (Q_i), and mass flowrate of molten salt (M) compared to both CPG processes. In addition, syngas yield nearly doubled, while by-products considerably decreased. The H_2:CO ratio increased more than 3 times, while the syngas/heat input ratio also nearly doubled. Clearly, the SPG processes were much more efficient for continuous solar gasification in molten salt. Comparison between the SPG in CLMS and its CPG counterpart reveals 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 pyrolysis process), whereas the corresponding values of 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 (McKetta et al., 1993.). In addition, the 88%-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 for CPG. Equally significant is the fact that total salt volume of SPG in CLMS (V_r = 37.5+123.6 = 161.1 m^3) was nearly half of its CPG counterpart (310.6 m^3) while total heat required was 12% less (24,832 kW vs. 26,814 kW).

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 product 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. It indicated that Ni/Al_2O_3 could actively catalyze the production of H_2 and CO, and reduced CH_4 yield even in high-temperature molten salt. The required total volume of molten salt storage for SPG in CLMS (V_r = 37.5+123.6 = 161.1 m^3) was 19% larger than SPG in MS (37.5+97.9 = 135.4 m^3). This could be ascribed to increased pyrolysis char yield (from 107 to 135 kmol/h) due to nickel catalyst in CLMS. Although the former required slightly larger total salt volume and total heat input than the latter, it showed much more attractive results in terms of syngas yields and quality. In conclusion, the SPG in CLMS could realize a more productive and economical process than the SPG in MS.

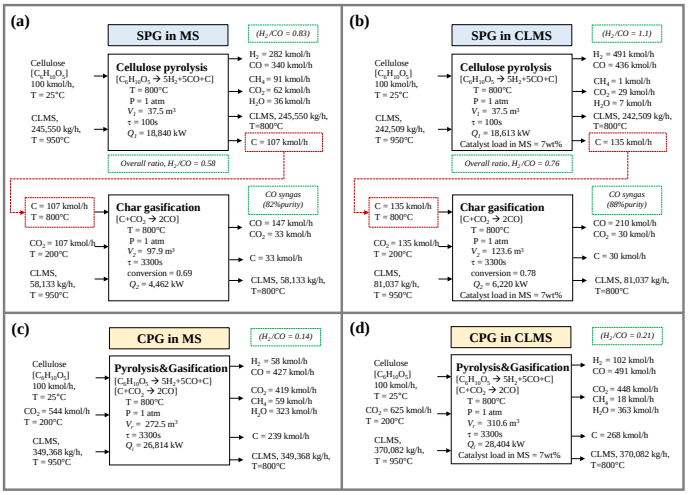

Fig. 3 Flow charts of (a) SPG in MS, (b) SPG in CLMS, (c) CPG in MS, and CPG in CLMS.

Table 2 Summary of key results from four conceptual process designs

Process	V_r [m^3]	Input				Output [kmol/h]						H_2/CO	Syngas/Heat [kmol/kW]
		M [kg/h]	Q_i [kW]	Cellulose [kmol/h]	CO_2 [kmol/h]	H_2	CO	CH_4	CO_2	H_2O	C		
SPG in MS	135.4	303683	23308	100	122	282	487	91	95	36	33	0.58	0.033
SPG in CLMS	161.1	323546	24832	100	135	491	646	1	59	7	30	0.76	0.046
CPG in MS	272.5	349368	26814	100	544	58	427	59	419	323	239	0.14	0.018
CPG in CLMS	310.6	370082	28404	100	625	102	491	18	448	363	268	0.21	0.021

Note: V_r = Total volume of molten salt with/without catalyst [m^3], $V_r = V_1+V_2$ for SPG process (see Fig. 3), M = Mass flowrate of molten salt with/without catalyst [kg/h], Q_i = Total heat input [kW], $Q_i = Q_1+Q_2$ for SPG process (see Fig. 3)

4. Conclusion

The Ni/Al_2O_3 catalyst significantly enhanced the syngas yield, reduced CH_4 yield, and increased char conversion. Both SPG processes required less total salt volume, total heat input, and mass flowrate of molten salt compared to both CPG processes. Syngas yield nearly doubled, while by-products considerably decreased, especially for CH_4. The H_2:CO ratio increased about 3 times, while the syngas/heat input ratio also nearly doubled. The required total reactor volume of SPG in CLMS was about half of its CPG counterpart. Similarly, the total heat required was 12% lower while the residual char decreased as much as 9 folds. Therefore, the SPG process in CLMS represented a promising process for high-quality syngas production with efficient solar energy utilization.

5. References

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