出國報告（出國類別：國際研討會）

出席 2012 年國際氫能會議心得報告

服務機關：國立中興大學 環境工程系

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摘要

本次國際氫能會議由韓國氫能源研發設計中心所主辦，其宗旨在於探討再生能源之技術與開發現況討論，著重於現今產氫技術之討論，透過國際各研究團隊產氫技術開發現況期望能提供一種潔淨且成本低廉的實廠產氫技術作為往後商業應用之借鏡。本次會議參與人員皆來自世界各地相關學術領域之研究團隊，其主辦地點為韓國首爾萬麗酒店，會議時間為 2012 年 6 月 24 日至 6 月 27 日，為期四天之研討會共計有 254 篇口頭報告與壁報展示，會議開幕演說由丁瑟教授主講題目為：創新能源解決方案於整合型產氫系統 以及日本三宅教授所主講之生物產氫發電的熵控制程序。吸引相當多國際學者前來聆聽。其後在研討會討論之過程中與其他國內外學者互相交換心得，相信可作為往後研究之寶貴經驗。

目次

一、　會議目的

本次 2012 國際氫能會議(international Conference on Hydrogen production, ICH2P)由韓國氫能源研發設計中心(Hydrogen Energy R&D center, HERC)所主辦，期為每年度舉辦一次之國際研討會議。本學術研討會之宗旨在於探討再生能源(Renewable Energy)之技術與開發現況討論，利用傳統石化燃料或是核子能源來製造產氫。而本次國際學術研討會則著重於現今產氫技術諸如熱化學產氫法(Thermochemical)、生物產氫法(Biological)、光化學或光電化學產氫法(Photochmical/Photoelectrochemical)之技術討論，透過國際各研究團隊產氫技術開發現況期望能提供一種潔淨且成本低廉的實廠產氫技術作為往後商業應用之借鏡。此外，該組織於 2009 年首次舉辦此氫能源國際研討會，對於該相關學術領域皆有相當程度之影響與貢獻。

二、　會議過程

1. 本次參與 2012 年韓國氫能國際研討會之研究團隊於 6 月 22 日提前抵達韓國首爾，預計在會議開始前除安置個人行李並搜尋會議場地與規劃行前路線外，同時利用時間交互進行口頭報告之練習與可能問題之演練，以求上台報告之穩定。

2. 本次會議參與人員皆來自世界各地相關學術領域之研究團隊，其主辦地點為韓國首爾萬麗酒店，會議時間為 2012 年 6 月 24 日至 6 月 27 日，為期四天之研討會吸引相當多國內外學者與會，在研討會討論之過程中與其他相關國內外學者互相交換心得，相信可作為往後研究之寶貴經驗。

3. 本次國際學術研討會始於 6 月 24 日開始進行註冊報到程序，而於 6 月 25 日開始進行多場學術演講與國內外學者報告。第一場的主題演講是由 Prof. Ibrahim Dincer 所主講的創新能源解決方案於整合型產氫系統其內容主要提及現今開發氫能的所可能遇到之問題以及新式產氫程序與實場之應用，其中現今實場應用與開發多以生物產氫與化學產氫方式為主，著重於開發程序上能源的平衡與經濟效應之考量為優先。在開場主題演講後緊接著就是分開之多場學術討論，其中本次所選擇參加的場次主題為「慣用產氫程序，Conventional Hydrogen Production, CHP」，由三位韓國學者與一位來自本校之博士班學生彭子桓發表口頭報告，其中一位韓國學者 Tae-Young Mun 所發表之主題為「以雙階段氣化流體化床與添加劑產生富氫且低焦油之氣體產物」與本人研究相近，其實驗乃利用雙階段流體化床反應器反應生成低焦油與高氫氣含量之合成氣體，實驗結果顯示在最佳的操作條件下可獲得約 88%的焦

油去除率以及約 32%的富氫氣之合成氣體，研究結果令人印象深刻，旋即於會後進行私下的心得交換與討論建議，相信對於後續實驗規劃與研究將更有幫助。

4. 後續參加的場次主題為「光化學產氫程序，Photochemical Hydrogen Production, PHP」分別由兩位印度籍學者與一位本校之博士班學生黃柄櫞所進行之口頭報告，主席為中國國家科學院院士李灿(Can Li)。第一位印度籍報告者為邀請演講，是由 Prof. V. DurgaKumari 所演講的題目是「Hydrogen production activities at Indian Institute of Chemical Technology」，內容說明目前印度國內對於產氫技術的發展與願景。其中黃同學所報告之主題為「Solar light induced photocatalytic hydrogen production over TiO_{2-x} $N_x/SrTiO_3$ nanocomposite」，獲得與會期間之熱烈討論，顯示國內新穎研究仍受國際矚目。最後由 Dr. Kumarsrinivasan Sivaranjani 所報告主題為「Mesoporous $TiO_{2-x}N_x$-nano Au composite: pseudo 3D material with visible light photocatalytic activity for Hydrogen generation」。於本場次結束後則進行午餐休息，大家可藉由午餐期間進行心得討論。

5. 於 6 月 26 日進行本次國際學術研討會之第三天行程，開場主題演講者為 Prof. Jun Miyake 所主講之題目為：「生物產氫發電的熵控制程序」，其內容講述目前生物產氫之實場應用現況與目前世界生物產氫團隊所研究之成果。爾後所參加之場次研究主題為「慣用產氫程序，Conventional Hydrogen Production, CHP」，主席是韓國亞洲大學(Ajou University) 的 Prof. Hyung-Taek Kim。本場次只有兩位報告者，另一位是來自於俄羅斯的學者 Marina Vernikovskaya 所主講有關利用觸媒轉化石化燃料合成氣為富氫氣與甲烷之氣體的經濟效益與其實場化評估。本次口頭報告即被大會編列於本場討論。

6. 於 6 月 26 日慣用產氫程序中為本次報告的場次，本次主講之題目為「以鋁、鈣抑制流體化床結塊去流體化於都市固體廢棄物氣化產氫之程序研究」，研究緣起在於流體化床反應器具有高熱傳與質傳效率以及高混合且爐內溫度易控制且分佈均勻，溫度變化小的優點，因此為目前經常使用於生質物氣化產氫之反應器選擇之一。但因其應用上的限制，容易結塊的物質在處理上會對於流體化床反應器造成去流體化的現象產生。許多文獻指出含有複雜且不純的物質可能會造成結塊現象的產生。而此種現象可能會造成流體化品質的下降以及去流體化現象。流體化床結塊是種複雜的現象，而可能造成結塊的原因很多，例如廢棄物的化學組成、以及流體化床的操作條件等等。結塊造成去流體化在操作上產生處理效率降低，產生污染物質的可能也相對增加，

對環境與人體健康的安危造成衝擊。部分學者整理後表示去流體化的機制可大略分為兩種型式：(1) 顆粒與顆粒本身物質的移動形成顆粒間的黏結部分：當其中的黏性力大於系統在流體化時所造成的分離力時，則結塊將生成，並可能導致去流體化的產生，當溫度越高或操作時間越長時，會使得顆粒將有越長的接觸時間而增加去流體化的機會。(2)反應過程中液態物質的產生：液態物質會在兩個顆粒中形成黏結部分，若其黏性力大於分離的力量時則結塊將生成，並造成去流體化。主要研究結果顯示添加 CaO、Al_2O_3、SiO_2 不同添加劑影響氣化過程中合成氣體之變化分佈；當分別添加不同添加劑時，其對 H_2 在氣狀產物所佔的分佈以添加 CaO 為產出最多，其次為 Al_2O_3，再者為 SiO_2 可得知；而 CO 在 Al_2O_3 加入後其值為最低；然而 CO_2 之產出以添加了 CaO 其排出量為最少，相關文獻指出添加 CaO 可降低 CO_2 的排放，主要原因有二：(1) 由於熱力學的緣故，CaO 可捕捉 CO_2 進而導致 H_2 產量的增加；(2) 加速焦油的裂解($Tar + n_1H_2O \rightarrow n_2CO_2 + n_3H_2$)另外在添加 Al_2O_3 之實驗結果得知氫氣與 CO_2 將會增加但 CO 則會有下降的趨勢，相關文獻亦指出添加氧化鋁將會提升氫氣的產量，主要原因在於添加氧化鋁有助於焦油與低碳數的有機物質裂解，進而產生氫氣，同時亦有學者提出焦炭反應屬吸熱反應，當溫度提升越高時，H_2 釋放越多，由反應式可得知。然而由反應式可得知 CO_2 跟 C 反應導致減少排出。而 CH_4 則因甲烷蒸氣反應得知，其反應式屬吸熱反應，此反應式中 CH_4 與水反應生成 H_2、 CO，故 CH_4 因溫度越高其排出隨之遞減，另外操作溫度由 700°C 增加至 950°C；其 char 由 21.08％降至 8.12%；氣體之產出量由 81.84%增加至 104.16％，本次研究數據與文獻中所提出之反應與趨勢皆相同。由此可得知當溫度上升時不但可增加 H_2 之產生也可降低 CO_2 之排出量。然而 CO 的降低可推測是由蒸汽重組反應(增加 CO 含量)與水氣轉移反應(消耗 CO 含量)二者反應的競爭結果，本次實驗並無額外添加水氣含量(基本水氣來源為空氣提供)，故主要反應將推測為消耗 CO 含量之水氣轉移反應為主。

7. 本次所報告之內容受主席與其他學者給予問題與相關意見，其中主席 Prof. Hyung-Taek Kim 提出建議流體化床的去流體化現象對於產氫程序上的三相質量平衡評估是分析產氫程序上十分重要的一環，以及另有國外專家學者提出如何評估流體化床去流體化程序以及本次實驗的後續應用為何，在討論的過程中針對建議的事項將會納入未來實驗目標的參考與評估，而其他學者對於本次報告的主題提出的相關問題也一一解答，同時也了解目前國內外學者專家所著重的研究方向以及對於所提問之問題也將反應於未來報告所該詳

細解釋之處，期望在後續參與國際研討會上能有更好的表現。在會後與其他相關學者交換心得，也針對未來研究方向做討論與建議，著實收穫不少。

8. 於 6 月 26 日晚間進行學術研討會晚宴，分別由研討會主辦人 Prof. Jong Won Kim 以及本次韓國氫能國際研討會的組織負責人 Prof. Ibrahim Dincer 與大家共進晚宴，其間並邀請韓國國內知名樂團替大家表演，著實增添不少輕鬆的氣氛。

9. 於 6 月 27 日的研討會行程，首先是由 Dr. Byung Ki Ahn 所主講之主題為「燃料電池車：最新可能性途徑」，主要說明針對高分子電極交換膜燃料電池(polymer electrolyte membrane fuel cell, PEMFC)應用於實際車輛的研究。而於 6 月 27 日的研討會最後行程排定為學術參訪，地點是在韓國核子氫氣工業。但由於參訪需額外費用，基於經濟方面考量故放棄本次學術參訪。

10. 適逢暑假期間，且本次研討會所發布之通知過晚導致本研究團隊未能於會議結束後即刻返國，原定 6 月 28 日之班機未能候補，因此將停留至 6 月 30 日(六)方能返台。此外，由於在會議期間曾與韓國首爾大學的 Dr. Tae-Young Mun 以及其研究團隊的 Mr. Cho-min Hucin 進行討論，彼此研究方向相似，故利用 6 月 29 日等待返國期間進行會後的研究討論，Dr. Tae-Young Mun 甫於韓國首爾大學能源與環境系統工程系畢業，其研究領域為流體化床氣化，以低焦油、高熱值為主的產物作為研究目標；目前之研究方向恰與 Dr. Tae-Young Mun 之研究領域相似，相信經過彼此意見交換後對於未來研究的細節與重點更能掌握。

11. 本次學術研討會區分相當多研究主題可供有興趣之學者參與及討論，其大會會議流程依不同日期與研究主題詳列如附件所示。

三、 會議心得

參與本次國際氫能會議舉辦之學術研討會除了增加環工與化工之相關專業知識外，亦可以與國內外學者互相討論。由討論的過程中獲益良多，也對於後續研究有相當大的幫助。參與國際性之學術研討會能讓自己了解不只是做實驗，而是要能將自己的成果報告，經過討論、批判方能精益求精。同時英文能力如聽、說、讀、寫等更是作為一個研究學者必備之能力，經過這次的研討會報告除了有相關之豐富經驗與專業領域的討論外，在參與國際研討會的同時也學習不同的報告方式、演說技巧等，以及主持人如何掌控會議都是以後可能會面對的狀況，從本次的研討會著實學習到不少相關訣竅。

四、 建議事項

首先很感謝教育部給予經費上之補助，能夠減少出國報告之負擔。本次前往韓國首爾參加國際性學術研討會，不僅是針對不同領域做相關之見習參訪之外，對於如何前往參與研討會的事前安排諸如食衣住行等也是一種生活技能上的學習，期望政府等相關單位能持續推動國內研究人才出國參加國際研討會之政策，以增進國內學者之國際觀。

附件

1. 參與國際學術研討會照片
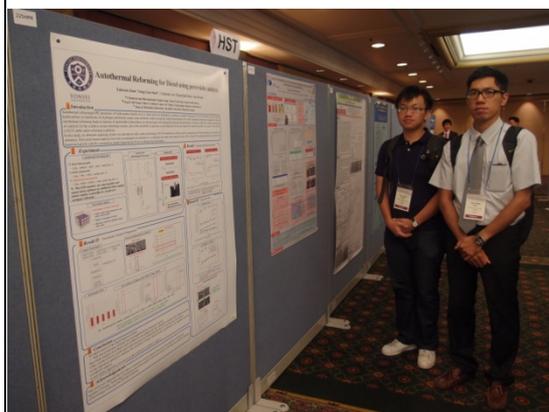
圖一、會議口頭報告	圖二、與會者討論
圖三、研討會現況	圖四、研討會地點外觀

HYDROGEN PRODUCTION DURING AIR GASIFICATION OF MODIFIED MSW UNDER AGGLOMERATION INHIBITION BY Al- AND Ca-BASED MATERIALS IN FLUIDIZED BED

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ABSTRACT

Biomass gasification is a sufficient and advanced technology for hydrogen production. However, biomass or waste usually contains alkali or earth alkali metals those may cause bed agglomeration which not only reduces the gasification/fluidization efficiency but also influences the emission of hydrogen production. Accordingly, the aim of this study focuses on the behavior of hydrogen production during air gasification of modified municipal solid wastes under particle agglomeration process. Moreover, the Al- and Ca-based materials have been added for the purpose of agglomeration controlling. The experimental results showed that defluidization occurred while alkali metal (sodium) was applied into system. Then, addition of CaO and Al_2O_3 can prolong the defluidization time significantly, and the inhibition level was following the sequence as Al_2O_3 > CaO. On the other hand, an increase trend of hydrogen production was found with two additives tested in fluidized bed system. The advantages of both agglomeration controlling and hydrogen production enhancement for those additives were confirmed in this study.

1. INTRODUCTION

Biomass gasification is renewable and a CO_2 neutral energy resource and fluidized bed was recognized as an important technique for using biomass. However, biomass gasification has a greater tendency towards bed material agglomeration. Agglomeration is caused by the combustion of wastes/biomass containing adhesion materials such as specific elements or plastics. Yan et al. described how the clinker probably formed at high temperature following the mechanisms of viscous flow sintering, and thus, crystalline transformation from quartz to cristobalite and tridymite might be indication of the ash agglomeration (Yan et al., 2005). Among the main species are those compounds with a low melting point, which may partially melt at low bed temperatures (500–600°C), thus causing bed material sintering. On the other

hand, Öhman and Nortin also discussed that melting of the coating was directly responsible for the bed agglomeration, and the melting behavior of the coatings was very sensitive to the relative amount of alkalis present that could be the main sintering promoters since their concentrations are relatively higher than other low melting point species found in the combustion system (Öhman and Nordin, 1998; Öhman and Nordin, 2000; Öhman et al., 2003). Thus, bed agglomeration occurred when wastes contained alkalis and thus became a serious problem for fluidized bed operation.

Some researchers have been done to investigate the mechanisms of bed material agglomeration during fluidized bed gasification processes (Kuo et al., 2010; Lin and Wey, 2004; Lin et al., 2003; Skrifvars et al., 1994; Steenari et al., 1998). Olofsson et al. found high content of alkali and alkaline earth metals exist in biomass material, and two possible mechanisms of particle agglomeration were reported (Olofsson et al., 2002): (1) homogeneous agglomeration: a slight agglomeration occurred on particle surfaces that resulted in an uniform particle size distribution of agglomerates. (2) Heterogeneous agglomeration: a fast increasing or variation of particle size of agglomerates led defluidization. K, Na, Si and Ca were assumed as sources of particle agglomeration, but Mg, Fe, Al were considered as inhibitors. Fryda et al. studied three different biomasses (giant reed、sweet sorghum bagasse、olive) during fluidized bed agglomeration process. The results indicated that agglomeration of giant reed and sweet sorghum bagasse due to theirs K-rich contents (Fryda et al., 2008). Additionally, Werther et al. illustrated the possible reactions during biomass/waste gasification because of alkali and alkaline earth metals react with bed materials:(Werther et al., 2000)

$$2SiO_2 + Na_2CO_3 \rightarrow Na_2O \cdot 2SiO_2 \text{ (m.p. = 874℃) + } CO_2 \tag{1}$$

$$4SiO_2 + K_2CO_3 \rightarrow K_2O \cdot 4SiO_2 \text{ (m.p. = 764℃) + } CO_2 \tag{2}$$
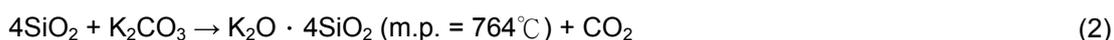
Besides, several additives were tested for reducing and controlling the bed agglomeration phenomenon. Elements such as Al and Ca were found to inhibit agglomeration in a fluidized bed. Previous studies have discussed that kaolin has been shown to be effective for deposit control, alkali vapor removal, and bed agglomeration control (Dahlin et al., 2006; Öhman and Nordin, 2000). Moreover, Ca-related additives have been used as alternative bed materials to control the agglomeration behavior (Tangsathitkulchai and Tangsathitkulchai, 2001). In addition, Bartels et al. summarized the control methods/strategies to prevent bed agglomeration included (1) operational actions, utilization of additives, and alternative bed materials (Bartels et al., 2008):

(1) Operational actions:

Lowering bed (operating) temperature, Temporary gas velocity increase, stopping the fuel feed with continued gas flow to break up agglomerates, optimizing the drainage of spent bed material and addition of fresh sand, and Pre-treatment of fuel.

(2) Utilization of additives:

      Addition of grindable particle, addition of silica sand of a different particle size, Al-Si-based clay materials, addition of Na-binding additive (kaolin, alumina, and gibbsite), and carbonates and oxides of alkaline earth metals (Ca, Mg, Ba).

 (3) Alternative bed materials:

      Al-related materials, alkaline earth metals-related materials, and others (Fe-, Zr-, Ni-related materials).

      Other research gruops also studied the control of agglomeration and defluidization during fluidized bed combustion. Their findings showed that sillimanite (Al_2SiO_5), limestone (Ca-rich), and bauxite (Al-rich) as alternative materials extended fluidized bed combustion operation without defluidization by 7–10 times compared to silica sand as the bed material (Vuthaluru et al., 1996; Vuthaluru et al., 1999; Vuthaluru and Zhang, 1999; Vuthaluru and Zhang, 2001). Similar results were observed from other research (Lin and Wey, 2004; Skrifvars et al., 1994; Fernández Llorente et al., 2006, 2008).Consequently, Al- and Ca-related additives were shown to be effective for particle agglomeration control.

      Above all, the aim of this study is to evaluate the effect of the Ca- and Al-based additives on particle agglomeration induced by modified alkali-containing municipal solid wastes (MSW) in fluidized bed air gasification. Under the process, the changes of syngas compositions which contain H_2, CO, CO_2 and CH_4 in each experiment are also considered.

2. EXPERIMENTAL

2.1 Apparatus

      Fig. 1 demonstrates the fluidized bed incineration system used in the experiments. The reactor is a bubbling fluidized bed incinerator made up of a preheated chamber (50 cm long) and a main chamber (105 cm high) with an inner diameter of 10 cm. The reactor is made of stainless steel (3 mm thickness, AISI 310) and is enclosed by an electrically resistant material packed with ceramic fibers to thermally insulate the system. The stainless steel porous plate functions as a gas distributor with a 15% open area. Three thermocouples are used to measure the temperatures of the preheated chamber, sand bed, and freeboard chamber.
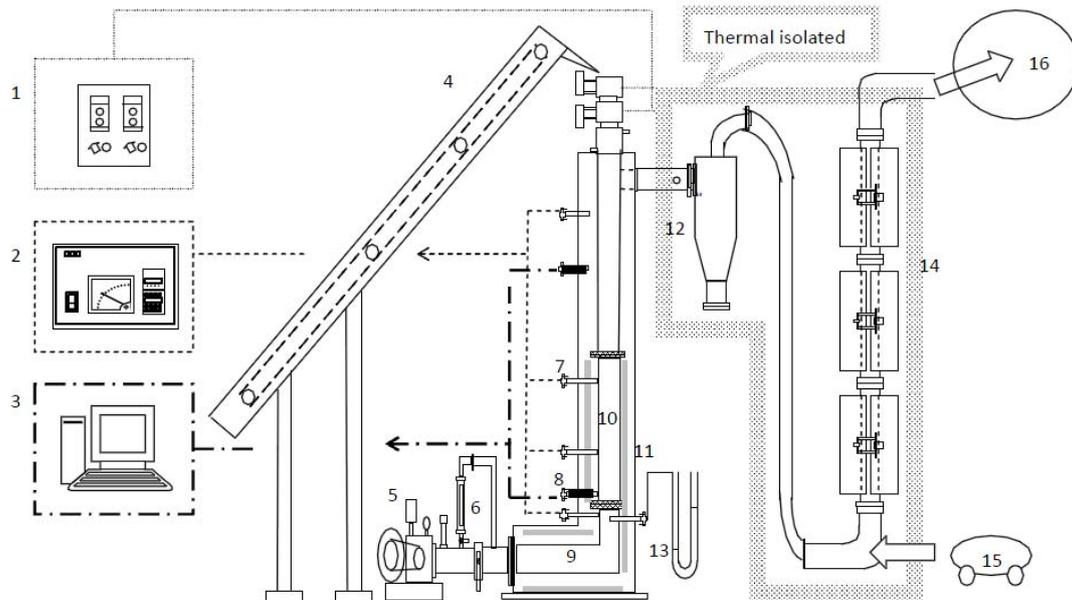
Fig.1. Bubble fluidized bed incinerator. (1) auto- feeder controller, (2) PID controller, (3) data collector, (4) auto-feeder, (5) blower, (6) flowmeter, (7) thermocouple, (8) pressure detector, (9) preheater chamber, (10) sand bed, (11) electric resistance, (12) sampling place, (13) U manometer, (14) secondary fluidized bed combustor, (15)secondary air supply, (16) induce fan.

The programmable logic controller is employed to control the temperature of the fluidized bed. Two pressure detectors are used to detect the difference between the pressure of the sand bed and the pressure of the freeboard chamber. These probes are connected to the different pressure transmitters (Huba control 692). The pressure signals are digitized and recorded by a data acquisition system (ADVANTECH PCLabCard PCI-1711 and ADAMView software). The pressure drop can be used to measure agglomeration during fluidization. According to previous studies, when the agglomeration condition occurs, a drastic increase in the temperature ensues as well as a simultaneous and rapid decrease in the bed pressure drop (Atakül et al., 2005; Siegell, 1984). Therefore, the pressure drop is used to measure agglomeration during fluidization. The secondary fluidized bed is set after the fluidized bed reactor to combust the exhaust organics behind the main gasifier, as shown in Fig. 1.

2.2 Preparing artificial feed wastes

The artificial solid waste included sawdust (2.25 g) and a polyethylene (PE) bag (0.3 g). The total mass was 3.55 g. An agglomeration promoter (Na) was added as nitrates ($NaNO_3$) with 1.2 wt% of one artificial waste pack. The metals to be investigated were dissolved as nitrates in distilled water, and the weight percentage of Na was calculated as atoms of the metal, not as nitrate. The metal solution (1 mL) was then added to the sawdust and was packed in a PE bag. Before the experiment, artificial wastes were stored for a day to ensure that the sawdust could absorb the metal solution completely. Silica sand, with an almost

constant density (ρp= 2600 kg/m^3), was used as the bed material in the experiment. The pressure-versus-time profile and visual observation were used to evaluate defluidization time.

2.3 Experimental procedure

When the sand bed temperature was in a steady state, and the artificial waste was fed into the chamber at the rate of 1 bag per 10 s, the pressure profiles were recorded to evaluate the rate of defluidization. The input air (relative to the theoretical air) was then used under the different operating temperatures. Input air at different ERs was determined. The ER is defined as the actual supply air divided by the stoichiometric air required for complete combustion.

Once the temperature of the sand (or sand + additive) became steady, the artificial waste was fed into the chamber at a rate of 1 bag per 10 s. The total amount of bed materials used was 1400 g. After each experiment, the combustion chamber was cooled down to room temperature, and the bed materials were collected. The different operating parameters employed, such as operating temperature, ER, and the amounts of bed materials, are presented in Table 1.

Table 1 Operating conditions in this study

Run	Type of bed composition	Addition of Na in waste	Sampling
1	SiO$_2$	None	Gaseous Products (H$_2$, CO, CO$_2$, CH$_4$)
2		Na with 1.2wt.%	
3	SiO$_2$+CaO	None	
4		Na with 1.2wt.%	
5	SiO$_2$+Al$_2$O$_3$	None	
6		Na with 1.2wt.%	

This experiment was divided into three parts. First, the operating parameters used, such as operating temperature (600, 700, 800, and 900 °C), ER (0.4, 0.5, 0.6, and 0.7), and amount of bed materials (1400, 1600, 1800, and 2000 g) under a Na ratio of 1.2 wt%, were changed. Gaseous products, such as H2, CO, CO2, and CH4, were sampled. After defluidization, the synthetic waste was continuously fed into the gasification chamber, and the products were then sampled.

Sampling and analysis

To capture the gaseous products, the tar and char should be removed. In this study, char was removed by a cyclone, and the tar was collected by the sampling procedure modified from the method of the Comité Européen de Normalisation-European Committee (CEN) for Standardization technical specification (CEN, 2011). The modified sampling chain was used in this study to collect the gaseous products, which were analyzed by gas chromatographer combined with thermal conductivity detector (GC/TCD).

3. RESULTS AND DISCUSSION

3.1 Effects of additive on gas composition

Figure 2 plots the effect of addition of additive on gaseous composition. Previous study presented that addition of CaO plays two important roles: (1) capturing CO$_2$ in syngas to improve the production of H$_2$ due to thermodynamic equilibrium. (2) Cracking of tar, accelerate the reaction between tar and H$_2$O as following equations (He et al., 2009a; He et al., 2009b):

$$C + H_2O \rightarrow H_2 + CO \quad \Delta H= 13138 \text{ kJ/kg mol carbon} \tag{3}$$

$$Tar + n_1H_2O \rightarrow n_2CO_2 + n_3H_2 \quad (\Delta H_{298}>0) \tag{4}$$

Chemical reactions can explain that addition of CaO leads the hydrocabonates react with H$_2$O to form H$_2$-rich syngas during gasification.
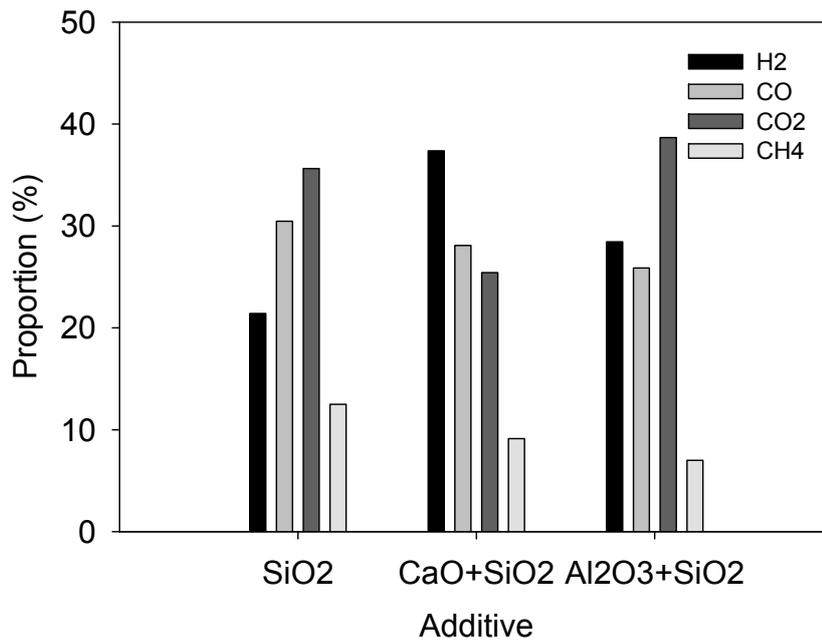
Fig.2. Effect of addition of additive on gaseous composition. (Operating condition: Temperature: 800℃, ER=0.5, amount of bed materials: 1400g; gas composition is calculated by N2-free environment)

3.2 Effects of additive (CaO, and Al_2O_3) on bed agglomeration during air gasification

Fig. 3 plots the defluidization time occurs at different bed materials during biomass air gasification. Addition of CaO and Al_2O_3 can prolong the defluidization time significantly, and the inhibition level is following the sequence as Al_2O_3 > CaO. It can be considered that addition of CaO and Al_2O_3 is an effective way to control the bed agglomeration in both incineration and air gasification environment. The results are in agreement of previous experimental results and papers (Corella et al., 1999a; Corella et al., 1999b).
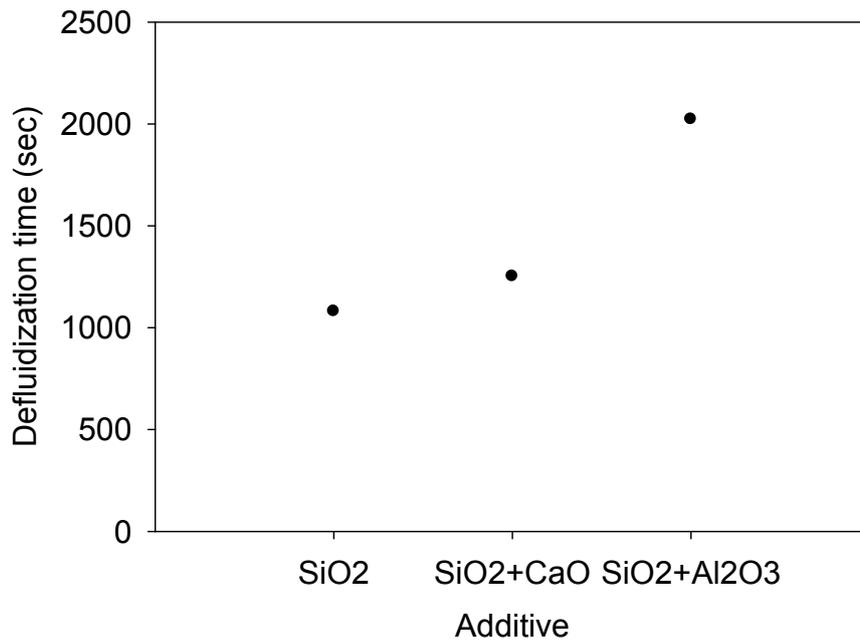
Fig. 3. Observation of defluidization time occurs at different bed materials during biomass air gasification

3.3 Effect of defluidization behavior on syngas composition.

On the other hand, the emission concentration and proportion of gaseous products are changed when system reaches to defluidization, as shown in Figure 4. A slight increase of emission concentration of H_2, CO and CH_4 under addition of CaO after defluidization, but emission concentration of CO_2 decreases. The proportion of each gaseous product also shows the same trend during defluidization process. However, emission concentration of CO_2 and CH_4 increases with addition of Al_2O_3, and there is no significantly change of emission concentration of H_2 and CO. The major differences between with/without additives are the changes of CH_4 during defluidization process, and it may be affected by particle agglomeration inhibits the CH_4 conversion efficiency of additives. In conclusion, applied additives such as CaO and Al_2O_3 those not only extend the tendency of bed agglomeration, but also influence the emission concentration of gaseous products after defluidization.
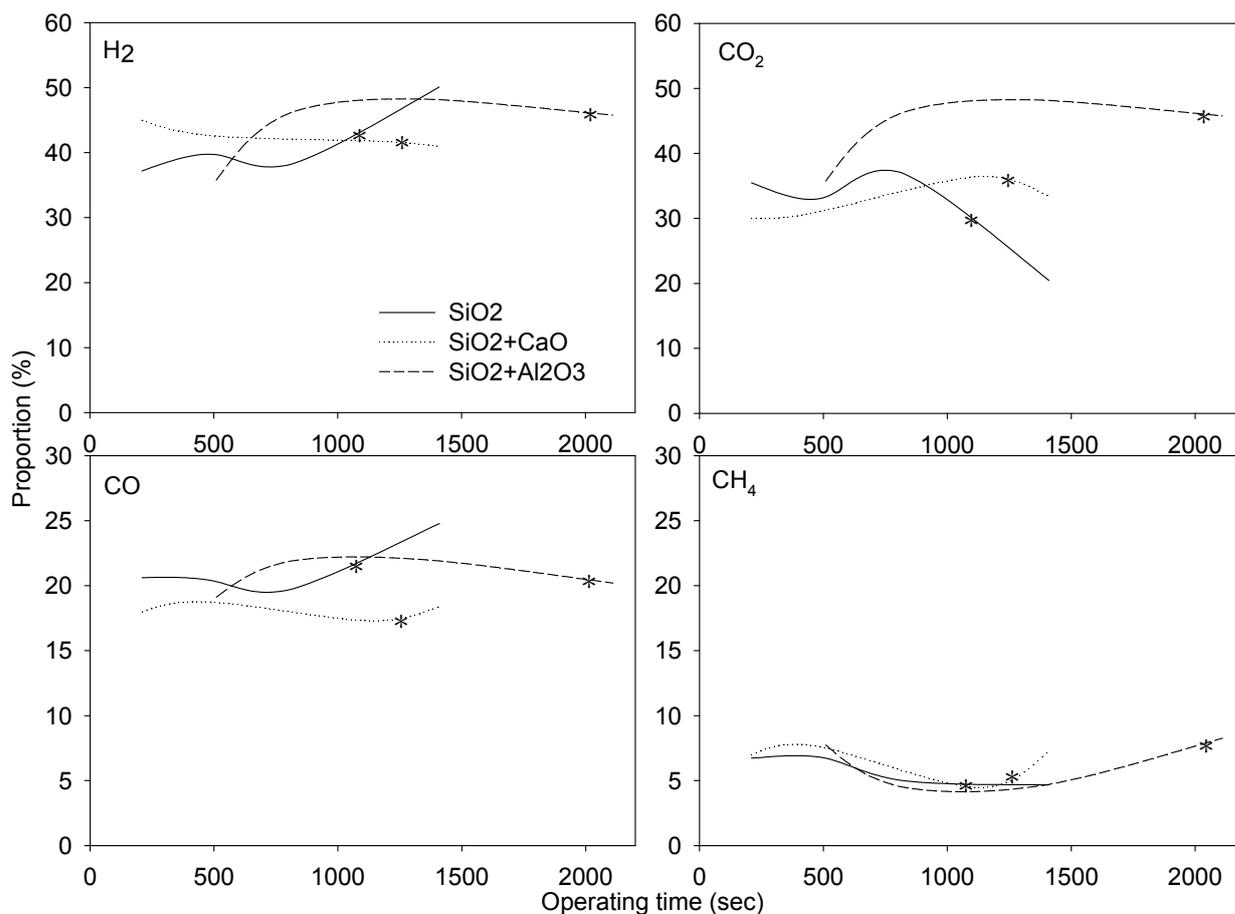
Fig.4. Effect of defluidization process on gas composition under addition of CaO and Al_2O_3. (Operating condition: Temperature: 800℃, ER=0.5, amount of bed materials: 1400g; gas composition is calculated by N_2-free environment; ∗, defluidization time)

4. CONCLUSIONS

The concentrations of gaseous products emitted with operating time are similar under various operating conditions such as temperature, air factor, and the amount of bed materials. The concentration and selectivity of H_2 and CO increases with operating time as agglomeration started, but CO_2 would reduce at that time. Besides, there is no significantly change for emission concentration of CH_4 in defluidization process. The reason can be explained that when system reaches defluidization, the fluidized bed system transferred to fix-bed state and the temperature increased on the surface of sand bed.

Applied additives such as CaO and Al_2O_3 those not only extend the tendency of bed agglomeration, but also influence the emission concentration of gaseous products after defluidization. The major differences between with/without additives are the changes of CH_4 during defluidization process, and it may be affected by particle agglomeration inhibits the CH_4 conversion efficiency of additives.

18

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