Toward Low-Temperature Coal Gasification: Experimental and Numerical Studies of Thermochemical Coal Conversion Considering the Interactions between Volatiles and Char Particles†

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Abstract
A novel triple-bed combined circulating fluidized-bed (TB-CFB) coal gasifier, consisting of a downer (pyrolyzer), a bubbling fluidized bed (gasifier), and a riser (combustor) was proposed for realizing low-temperature coal gasification. Several key thermochemical reactions were extracted from those expected in the downer unit: the reforming of refractory tar in both the gas phase and over the char surface, and the steam gasification of the nascent char. This review highlights our recent progress, both experimental and numerical, in studies of thermochemical coal conversion including the various reaction processes, by employing a drop-tube reactor that well approximates the reaction environment in a downer reactor. This discussion can be utilized in designing TB-CFBs and optimizing their operation.

Keywords: coal gasification, simulation, fluidized-bed reactor, tar reforming, drop-tube reactor, reactor modeling

1. Introduction
Coal plays an important role in meeting current world energy demands, and should continue to do so in the near future. The development of techniques for the higher-efficiency clean utilization of coal, such as coal gasification, is becoming an increasingly active area of research (Li C.Z., 2006). Currently, many coal gasification technologies are based on partial combustion at temperatures above 1200 °C. High temperature provides significant advantages for realizing the very fast thermochemical conversion of coal into syngas, but also offers the added expense of chemical energy of the fuel due to heating. The cold gas efficiency can be raised theoretically further by decreasing O2 consumption while increasing steam or CO2 consumption, which would result in gasification operations at lower temperature. Low-temperature gasification with higher cold gas efficiency has received widespread attention in recent years (Hayashi et al., 2014).

The low-temperature gasification of coal is conducted at temperatures well below 1000 °C. Fixed- and fluidized-bed gasifiers, as the main reactor systems for low-temperature gasification, have been developed toward the commercial production of power. The low temperatures, however, inevitably result in slower coal conversion into syngas. The novel Lurgi fixed-bed gasifiers suffer from high tar yields in the product gases (Li X.T. et al., 2004), and the processing rates are slow compared with entrained- and fluidized-beds (Hobbs et al., 1993). Fluidized beds now find wide application in coal gasification (Li X.T. et al., 2004). However, due to their high degree of solids mixing and particle entrainment, a single fluidized bed cannot achieve high solids conversion, as observed with the U-gas® gasifier (Goyal and Rehmat, 1992). Therefore, it is necessary to develop a novel gasification technology with higher cold gas efficiency.

Recently, a triple-bed combined circulating fluidized-bed reactor (TB-CFB) system, consisting of a downer (pyrolyzer), a bubbling fluidized bed (BFB, gasifier), and a riser (combustor), as shown in Fig. 1, was proposed.
In brief, the downer was added to a dual-bed circulating fluidized reactor system, after the riser (combustor) and before the BFB gasifier. Fresh coal was fed, mixed with hot circulating solids for the riser, including recycled char and the circulating medium, and rapidly pyrolyzed in the downer at around 900°C. The resultant tar was simultaneously and rapidly decomposed into syngas and/or coke over the nascent and recycled chars. Then, the tar-free char was separated from the syngas, sent to the BFB gasifier, and gasified without the negative effect of the volatiles-char interaction. The char gasification and volatiles reforming are thus expected to be decoupled under this reactor system. The endothermic and exothermic processes were separated in this system to realize the concept of low-temperature gasification with high cold gas efficiency.

As one important part of the reactor system, the novel downer reactor was expected to decompose tar and thus avoid the detrimental effects of tar on the subsequent char gasification and downstream system operation. After the coal is fed, coal, char particles, and gases flow concurrently in the downer. Several key thermochemical reactions were extracted from the coal conversion involved in the downer: the reforming of tar, the steam gasification of the nascent char, and complex interactions between the volatiles and char. The focus of this review is to highlight our recent understanding of thermochemical coal conversion in the downer reactor of the TB-CFB system, together with some future perspectives.

2. In situ tar reforming process

Tar, an undesirable product of gasification, is defined as the products heavier than C₆ compounds, such as benzene, that can be condensed at ambient temperature. Its reforming is mandatory for power generation and liquid production (Hayashi et al., 2014). Liquid scrubbing techniques and catalytic reforming methods suffer from undesirable overall thermal efficiency loss and/or catalyst deactivation because of the deposition of chlorine/sulfur compounds and carbon (Abu El-Rub et al., 2004a; Devi, et al., 2002; Simell et al., 1997). Thus, it is necessary to develop a tar reforming system with high thermal efficiency and without catalyst poisoning or deactivation. The effective decomposition of tar compounds over biomass/coal-derived chars has been frequently reported (Abu El-Rub, 2008; Gilbert et al., 2009; Krerkkaiwan et al., 2015; Krerkkaiwan et al., 2013; Sun et al., 2011). Naphthalene, representative of the most refractory compounds among tar constituents, was decomposed almost completely over chars or charcoals from different biomass/coals within a short gas residence time (less than 0.25 s) in a fixed-bed reactor (Abu El-Rub, 2004b; Fuentes-Cano et al., 2013). Except for benzene and naphthalene, tar constituents were completely decomposed over the coke accumulated in nanoporous alumina within a gas residence time of 0.03 s (Hosokai et al., 2005). These studies demonstrate the potential of utilization of char for tar elimination.

The in situ tar reforming process is one of the key thermochemical phenomena in the downer reactor of the TB-CFB system. Matsuhara et al. (2010) used a two-stage reactor to realize the in situ reforming of nascent tar from the rapid pyrolysis of brown coal over char obtained from the same coal. The results showed that the released tar can be decomposed over the char completely at 900°C. This indicated the potential for the rapid and complete decomposition of tar over a char surface due to an intensive tar-char interaction. However, the characteristics of the char and reaction conditions of the two-stage reactor system are different from those of the downer reactor, through which coal, char particles, and gases are concurrently flowing. In the downer reactor, the in situ reforming of nascent tar occurs over the nascent char from the rapid pyrolysis of the same coal. In addition, it is not possible to use a fixed char bed to realize the decomposition of tar in the continuously operating TB-CFB system.

In our recent study (Zhang et al., 2013b), a drop-tube reactor (DTR) was employed to simulate reaction environments similar to those in the downer reactor. An
Australian brown coal (Loy Yang, hereafter referred to as LY) was co-fed with char (LYC) or partially gasified char (GLYC) into the DTR, and the effects of the char proper was co-fed with char (LYC) or partially gasified char (GLYC) fed into the DTR. The differences between their yields are direct evidence of nascent tar decomposition through intensive tar-char interactions. Coking/coke gasification and direct steam reforming are two current possible mechanisms proposed to explain the phenomenon in which the tar is decomposed over the char surface (Hosokai et al., 2008; Matsuhara et al., 2010). It is more reasonable that coking gasification is the main contributor to nascent tar decomposition over a char surface in non-catalytic tar reforming, compared with the direct steam reforming of tar, because the direct steam reforming reactions occur to a lesser extent than coking if catalysts are not used. The nascent tar from the pyrolysis of LY was decomposed by coking over the char from the flash pyrolysis of the same coal, and the char/coke was simultaneously gasified with steam. The steam gasification of the char/coke created new active sites to maintain the tar coking over the char surface. It is noted that the direct steam gasification of tar also is an important role of in situ tar reforming. LY contains abundant Na⁺ and Ca²⁺, and these alkali and alkaline earth metal (AAEM) species that remain in the resultant char are considered to play catalytic roles in the steam gasification of char/coke. This means that higher AAEM contents would be favorable for maintaining the coking activity of the char, and thus, to some extent, the higher coking activity of the char would promote more tar conversion into soot/coke over the char surface.

3. In situ steam gasification of char gasification

The steam gasification of char, as a gas-solid thermochemical conversion, is the rate-determining step (Mühlen et al., 1985) for the entire coal gasification process. The process has been studied by many researchers to understand the kinetics and mechanisms of both non-catalytic and catalytic reactions using fixed- (Haga and Nishiyama, 1988) and fluidized-bed reactors. H₂ is the main inhibitor in the steam gasification of char (Lussier et al., 1998; Yang and Duan, 1985); the rate of steam gasification in the presence of H₂ is lower by an order of magnitude or more than in its absence. However, recent studies (Hayashi et al., 2000, 2002) have shown that pyrolysis-derived volatiles, including tar, are much stronger inhibitors than H₂ in the steam gasification of char, because of the volatiles-char interactions.

The gasification of AAEM-loaded coals has been investigated. Bayarsaikhan et al. (2005) found that the inherent Na⁺ and Ca²⁺ species increased the initial gasification rate of the nascent char under a steam atmosphere by more than 80 % in a drop-tube/ fixed-bed reactor system. Mašek et al. (2009) reported that catalytic steam gasification proceeded extensively even under conditions in which the gasification of the unloaded coal was retarded by coexisting tarry compounds and char. In addition, higher AAEM contents have also been shown to be favorable for maintaining the coking activity of the char, promoting the in situ steam reforming of tar over the char surface. Therefore, the in situ steam gasification of AAEM-loaded char under volatiles-char interactions is worth studying.

AAEM species are generally loaded on low rank coals using water-soluble precursors such as NaCl (Takarada et al., 1989; Wu et al., 2005), Na₃NO₃ (Yamashita et al., 1991), Ca(NO₃)₂ (Ohtsuka and Tomita, 1986), CaCl₂ (Yamashita et al., 1992), Ca(CH₃COO)₂ (Ohtsuka and Tomita, 1986; Tyler and Schafer, 1980), KCl (Liu and Zhu, 1986), or K₂CO₃ (Liu and Zhu, 1986; Tristantini et al., 2015). Kajita et al. (2010) reported that Na⁺ and K⁺ were irreversibly transferred from the char to the mineral matter (alumina) when contacting with each other at 800 °C. Irreversible reactions between the AAEM and fluidizing medium/circulating medium not only diminish the catalytic action, but also bring about problems in downstream...
Operations. For example, the defluidization and agglomeration of bed materials occur in fluidized beds because of the formation of Na/K silicates with melting point temperatures below 1000 °C. Therefore, Ca-containing materials are the most promising catalyst precursors for the steam gasification of char. It is noteworthy that a slurry of coal and water usually becomes acidic as a result of the dissolution of organic acidic compounds from brown coal. CaCO₃ and Ca(OH)₂ (which become more soluble in the slurry) have also been reported for use as catalysts in the steam gasification of char (Kim et al., 2013; Ohtsuka and Asami, 1996, 1997; Ohtsuka and Tomita, 1986). Ohtsuka et al. (1997) reported that the catalytic activity of Ca²⁺ from CaCO₃ was higher than that from Ca(OH)₂ in a thermobalance reactor. The reported results, however, were obtained at a low heating rate; the reactor system could not provide a heating rate as high as that achieved in the downer reactor for coal gasification. The higher heating rate causes more rapid thermal cracking and provides more active sites on the char particles for steam gasification. AAEM species can better catalyze the gasification of nascent char, as well as the in situ reforming of volatiles over the char surface, even in a short reaction time. Ca-catalyzed gasification is also known to slow as the process of char conversion proceeds (Liu and Zhu, 1986; Ohtsuka and Asami, 1996, 1997). Possible mechanisms include the sintering of CaO or Ca₂⁺ from these inexpensive materials on the in situ steam gasification of char. It is noteworthy that a slurry of CaCO₃ and Ca(OH)₂ (which become more soluble in the steam gasification of char) results for AD-3.2%Ca and AD-0.52%Ca (of initial Ca content in the AD-0.52%Ca was only about 1/6 that in the AD-3.2%Ca, the activity seemed to be lower, with only about 1/6 of that in the AD-3.2%Ca, the activity seemed to be equivalent with that in the AD-3.2%Ca at 950 °C, and thus, even higher at 1000 °C. This means that both the specific and overall activities of Ca were reduced by increasing the Ca loading on the AD from 0.52% to 3.2% for in situ steam gasification at 950–1000 °C.

The X_char value increases in the order AD < AD-Na < AD-Ca < AD-Ca-Na, indicating that AD-Ca-Na had the highest reactivity under the current conditions. Some other studies (Ohtsuka and Tomita, 1986; Takarada et al., 1989) reported that the Na in Australian brown coal at 650 °C exerted a smaller catalytic effect than Ca in the same coal at the same catalyst content (5%).

The X_char results for AD-3.2%Ca and AD-0.52%Ca (of which concentrations of Ca are 3.2 and 0.52 wt%, respectively) show that the Ca²⁺ in the former was more active than that in the latter at 900 °C, but less active at 1000 °C. It is generally accepted that the activity of AAEM catalysts increases with increasing loading and then levels off at a certain point. Increases in the catalyst concentration tend to bring about increases in the size of the catalytic particles, coarsening them through agglomeration and/or coalescence. Thus, a higher Ca content causes more facile coarsening of the catalyst particles (Cazorla-Amoros et al., 1993; Radovic et al., 1983). In addition, although the initial Ca content in the AD-0.52%Ca was only about 1/6 of that in the AD-3.2%Ca, the activity seemed to be equivalent with that in the AD-3.2%Ca at 950 °C, and thus, even higher at 1000 °C. This means that both the specific and overall activities of Ca were reduced by increasing the Ca loading on the AD from 0.52% to 3.2% for in situ steam gasification at 950–1000 °C.

It is noteworthy that X_char for AD-3.0%Ca-0.36%Na was as high as 71% and much higher than that for AD-3.2%Ca, although their Ca contents were nearly equivalent. Compared with catalytic effect of AD-1.5%Na, the difference in X_char between AD-3.0%Ca-0.36%Na and AD-3.2%Ca is attributed mainly to either the activity of Na or synergy due to the coexistence of Na and Ca that could suppress the coarsening of the Ca catalyst particles.

$$X_{\text{char}} = \frac{(\text{primary char yield}) - (\text{char yield from DTR})}{\text{primary char yield}} \times 100\%$$

X_char is the difference in the extent of carbon deposition between the char and steam gasification of char carbon together with the deposited carbon. Fig. 3 shows X_char as a function of temperature. X_char for AD at 900–950 °C is less than 10%, and catalysis by the inherent AAEM species, if any, was insignificant. However, X_char for the catalyst-loaded coals was in the range from 15 to 45%, and the process of steam gasification within 3 s was clear.
Coal conversion incorporating the volatiles-char interactions proceeds via a number of complex parallel reactions, and produces a wide range of products such as char, soot, light hydrocarbons, and both single and polycyclic aromatic hydrocarbons. The volatiles-char interaction has been frequently reported for different reactor systems, and the results show that the interaction has a significant role in inhibiting char gasification and promoting nascent tar decomposition. (Hayashi et al., 2014; Li C.Z., 2013). However, those studies focused on laboratory-based experimental investigations only. Kajitani et al. (2013) proposed a kinetic model incorporating the volatiles-char interaction, which reproduced the experimental findings from coal conversion very well, including the effects of the Na concentration in the char during steam gasification. It can also be used in designing any industrial fluidized-bed gasifier in the presence of volatile-char interactions. Although no studies have been performed, the development of a mathematical model based on the experimental results for coal conversion, including the volatiles-char interactions in the downer reactor of a TB-CFB system, should be considered.

4.1 Kinetic model

The lumping component model, an approach in which complex mixtures with large numbers of compounds are lumped into smaller groups of pseudo-components, is widely employed to provide a tractable number of kinetic equations and estimate kinetic parameters. To date, it has been mainly applied in investigations of hydrogenation or the catalytic cracking of heavy oil (Lan et al., 2009; Theologos and Markatos, 1993).

In our recent study (Li C.Y. et al., 2015), it was employed for the first time to estimate kinetic parameters in complex coal conversion environments, including volatiles-char interactions, which were approximated for the downer reactor of the TB-CFB system. A network among lumps in the DTR is proposed as shown in Fig. 4. Under our conditions, it is assumed that the coal sample has already been converted into tar, carbon gases, char, and soot by primary pyrolysis at the top non-isothermal zone of the DTR (at 500–900 °C) (Jamil et al., 2004; Sathe et al., 1999). The carbon conversion reactions in the isothermal zone of the DTR were simulated, and the feedstock was lumped into tar, carbon gases, char, and soot derived from the primary pyrolysis of the coal. The possible main reactions in the DTR were considered to be thermal cracking/steam reforming of the volatiles, gasification, and the volatiles-char interactions. The kinetic parameters of the four-lump model were estimated through a mathematical model integrated with a four-order Runge-Kutta method.

4.2 Kinetic model coupled with a computational fluid dynamics (CFD) approach

In the downer reactor of the TB-CFB system, coal, char particles, and gases flow concurrently. Gas-solid two-phase mixed flows are key phenomena and of particular interest for understanding the downer reactor. Ropelato et al. (2005) proposed an Eulerian-Eulerian approach for predicting fluid dynamics in the downer reactor, with good agreement between the experimental data and model predictions. Fushimi et al. (2012) also used an Eulerian-Eulerian method to investigate the degree of solid-solid mixing in the downer unit by simulating the hydrodynamics of hot sand, cold sand, and air, as well as the heat transfer among them. The simulation results agreed well with the experimental observations. An Eulerian-Lagrangian method (CFD-DEM) was applied by Zhao et al. (2007) to simulate gas-solid flows in a 2-dimensional downer reactor, and the predicted macro-scale flow structure had good agreement with the experiments. The published works can successfully predict fluid dynamics in the downer reactor with good agreement between experimental data and model predictions. The data can be useful, but the models only include numerical simulations of gas-solid flows in the downer reactor for coal conversion without considering the chemical reactions. Thus, a CFD approach for gas-solid flows combined with a chemical kinetic model for coal conversion that accounts for the volatiles-char interactions in the downer reactor is urgently needed. An Eulerian-Eulerian model was employed to simulate the fluid dynamics of gas-solid flow environments approximated for the downer reactor. Six global chemical
reactions with the corresponding kinetics parameters derived from the lumping model were considered in the simulation. The proposed CFD model gave acceptable predictions of gas-solid flows with carbon conversion reactions in the DTR in the presence of volatiles-char interactions (Li C.Y. et al., 2015).

The mass fraction distribution of the four lumps obtained from the simulation is illustrated in Fig. 5. In the carbon thermo-conversion process, in situ reforming of tar over the char surface occurred, and resulted in the mass fraction of tar decreasing gradually from inlet to outlet. For char particles, steam gasification is a main pathway for conversion, and their mass fraction also decreases. In contrast, the mass fraction of carbon gases increases very quickly along the DTR. This can be explained by the production of carbon gases through tar cracking and the gasification of both char and soot, which occur at faster rates than that of tar pyrolysis to produce tar.

In addition, the effects of reaction temperature, solid hold-up, and steam partial pressure on tar consumption along the DTR are shown in Fig. 6. It is very clear that about 85% of the tar is consumed at a rapid rate near the DTR entrance zone. Furthermore, the reaction temperature and solid hold-up are two significant factors in tar decomposition, whereas the steam partial pressure has little effect.

5. Conclusions

This manuscript describes the potential of the downer reactor for coal conversion, including tar reforming and char gasification, in a triple-bed combined circulating fluidized-bed reactor system. A drop-tube reactor was employed to simulate the reaction environment approximated in the downer reactor, wherein coal, char particles, and gases are concurrently flowing. Increasing the reaction temperature, feeding rate, and char concentration enhanced the tar decomposition. Inexpensive raw materials such as Na2CO3 and Ca(OH)2 effected good catalytic performance for the steam gasification of the char. Finally, a kinetic model with four lumps (gases, tar, char, and soot) and six reactions encompassing the volatiles-char interactions was developed and successfully integrated with a CFD approach to simulate the gas/particle flow in the DTR.

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![Fig. 5](Fig. 5 The contours of different lumps derived from the CFD simulation (in run 4, (a) carbon gases; (b) tar; (c) char; (d) soot. Sum of mass fractions of gas phases = 1; Sum of mass fractions of solid phases = 1) Reprinted with permission from Ref. (Li C.Y. et al., 2015). Copyright: (2015) Elsevier B.V.)
ship Council (CSC Program) and the Kyushu University Global COE program (G-COE Program). The authors are grateful to Professor Hsiu-Po Kuo and Dr An-ni Huang at Department of Chemical and Materials Engineering, Chang Gung University, Taipei for their valuable suggestions for mixed phase flows.

Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>AAEM</td>
<td>alkali and alkaline earth metal</td>
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<tr>
<td>AD</td>
<td>Adaro coal</td>
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<tr>
<td>BFB</td>
<td>bubbling fluidized bed</td>
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<tr>
<td>CFD</td>
<td>chemical fluid dynamics</td>
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<td>DTR</td>
<td>drop-tube reactor</td>
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<tr>
<td>GLYC</td>
<td>partially gasified Loy Yang coal char</td>
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<td>LY</td>
<td>Loy Yang coal</td>
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<td>LYC</td>
<td>Loy Yang coal char</td>
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<tr>
<td>TB-CFB</td>
<td>triple-bed combined circulating fluidized-bed reactor</td>
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<tr>
<td>$X_{\text{char}}$</td>
<td>net conversion of the primary char</td>
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References


Author's short biography

Cheng-Yi Li

Cheng-Yi Li received his PhD by accomplishing a study on modelling and simulation on reacting flow included in thermochemical conversion process of coal in 2015 at Kyushu University. He received his bachelor and master degrees at China University of Mining and Technology (Beijing) and currently working at China Tianchen Engineering Corporation as a process engineer for designing and developing advanced chemical plants in different fields, such as coal gasification plant, petrochemical plant and so on.

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